



### DECLARATION

I, Mari Kawanishi, a staff member of TAIYO, NAKAJIMA & KATO, 3-17, Shinjuku 4- chome, Shinjuku-ku, Tokyo 160-0022, Japan, do hereby declare that I am well acquainted with the English and Japanese languages and I hereby certify that, to the best of my knowledge and belief, the following is a true and correct translation made by me into the English language of the documents in respect of Japanese Patent Application No. 2002-367663, that was filed on 19th December 2002 in the name of FUJI PHOTO FILM CO., LTD..

Dated this 24th day of June, 2005

*Mari Kawanishi*

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[DOCUMENT NAME] SPECIFICATION

[TITLE OF THE INVENTION]

PHOTOTHERMOGRAPHIC MATERIAL AND  
IMAGE FORMING METHOD USING SAME

[WHAT IS CLAIMED IS]

[Claim 1] A photothermographic material comprising, on a surface of a support, an image-forming layer comprising at least a photosensitive silver halide, a non-photosensitive organic silver salt, a reduction agent for a silver ion, and a binder,

wherein: 1) a silver iodide content in the photosensitive silver halide is in a range from 40 mol% to 100 mol%; and 2) an average sphere-equivalent diameter of the photosensitive silver halide is in a range from 0.3  $\mu\text{m}$  to 5.0  $\mu\text{m}$ .

[Claim 2] The photothermographic material of claim 1, further comprising a compound which after thermal development substantially reduces visible light absorption caused by the photosensitive silver halide.

[Claim 3] The photothermographic material of claim 2, further comprising a silver iodide complex forming agent as the compound which after thermal development substantially reduces visible light absorption caused by the photosensitive

silver halide.

[Claim 4] The photothermographic material of any one of claims 1 to 3, wherein the photosensitive silver halide is contained as tabular silver halide grains having an aspect ratio of no less than 2.

[Claim 5] The photothermographic material of any one of claims 1 to 4, wherein at least 50%, in terms of a projected area, of the photosensitive silver halide grains is occupied by tabular grains having an aspect ratio of from 2 to 50.

[Claim 6] The photothermographic material of any one of claims 1 to 5, wherein the average sphere-equivalent diameter of the photosensitive silver halide is in a range from 0.5  $\mu\text{m}$  to 3.0  $\mu\text{m}$ .

[Claim 7] The photothermographic material of any one of claims 1 to 6, wherein the photosensitive silver halide contains silver iodide in an amount from 70 mol% to 100 mol%.

[Claim 8] The photothermographic material of any one of claims 1 to 7, wherein the photosensitive silver halide contains silver iodide in an amount from 80 mol% to 100 mol%.



[Claim 9] The photothermographic material of any one of claims 1 to 8, wherein the photosensitive silver halide contains silver iodide in an amount from 90 mol% to 100 mol%.

[Claim 10] The photothermographic material of any one of claims 1 to 9, wherein the silver iodide complex forming agent is a compound represented by one of the following formulas (1) and (2):

[Formula 1]

Formula (1)



Formula (2)



wherein, in the formula (1), Y represents a non-metallic atomic group necessary for forming a 5- to 7-membered heterocycle containing at least one of a nitrogen atom and a sulfur atom;

the heterocycle formed by Y may be saturated or unsaturated, or may have a substituent; and

substituents on the heterocycle formed by Y may be combined with each other to form a ring; and

wherein, in the formula (2), Z represents a hydrogen atom or a substituent;

n represents an integer of 1 or 2,

when n represents 1, S and Z are combined with each other by a double bond;

when n represents 2, S and each of two Zs are combined with each other by a single bond;

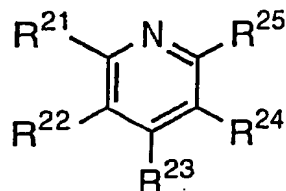
when n represents 1, Z does not represent a hydrogen atom; and

when n represents 2, two Z's may be same as, or different from, each other, but neither of the two Zs represents a hydrogen atom.

[Claim 11] The photothermographic material of claim 10, wherein the compound represented by the formula (1) is a pyridine derivative represented by the following formula (3):

Formula (3)

[Formula 2]

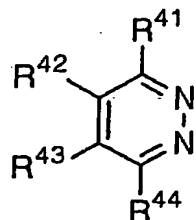


wherein  $R^{21}$  to  $R^{25}$  each independently represent a hydrogen atom or a substituent and may be combined with one another to form a saturated or unsaturated ring.

[Claim 12] The photothermographic material of claim 10, wherein the compound represented by the formula (1) is a pyridazine derivative represented by the following formula (4):

Formula (4)

[Formula 3]



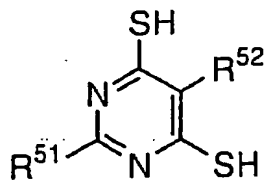
wherein R<sup>41</sup> to R<sup>44</sup> each independently represent a hydrogen atom or a substituent and may be combined with one another to form a saturated or unsaturated ring.

[Claim 13] The photothermographic material of claim 10, wherein the compound represented by the formula (1) is a 5- to 7-membered heterocycle having at least one mercapto group as a substituent and having at least one of a nitrogen atom and a sulfur atom.

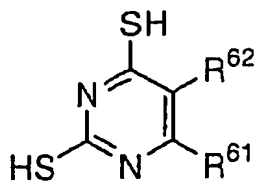
[Claim 14] The photothermographic material of claim 10, wherein the compound represented by the formula (1) is a compound represented by one of the following formulas (5) to (7):

[Formula 4]

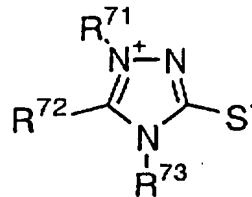
Formula (5)



Formula (6)



Formula (7)



wherein R<sup>51</sup> and R<sup>52</sup>, R<sup>61</sup> and R<sup>62</sup>, and R<sup>71</sup> to R<sup>73</sup> each

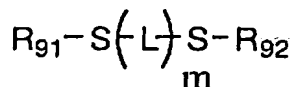
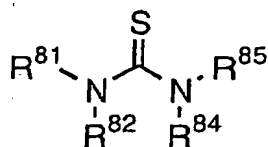
independently represent a hydrogen atom or a substituent.

[Claim 15] The photothermographic material of claim 10, wherein the compound represented by the formula (2) is a compound represented by one of the following formulas (8) and (9):

[Formula 5]

Formula (8)

Formula (9)



wherein  $\text{R}^{81}$  and  $\text{R}^{85}$ , and  $\text{R}^{91}$  to  $\text{R}^{92}$  each independently represent a hydrogen atom or a substituent; L represents a divalent linking group; and m is 0 or 1.

[Claim 16] The photothermographic material of any one of claims 10 to 14, wherein the compound represented by the formula (1) is a nitrogen-containing heterocyclic compound, and an acid dissociation constant (pKa) of a conjugate acid thereof in a tetrahydrofuran/water (3/2) mixed solution at 25°C is preferably in a range from 3 to 8.

[Claim 17] The photothermographic material of any one of claims 10, 11 and 16, wherein the compound represented by the formula (1) is the pyridine derivative represented by the formula

(3), and an acid dissociation constant (pKa) of a conjugate acid thereof in a tetrahydrofuran/water (3/2) mixed solution at 25°C is preferably in a range from 3 to 8.

[Claim 18] The photothermographic material of any one of claims 1 to 17, further comprising at least one type of phthalic acid or a derivative thereof.

[Claim 19] The photothermographic material of any one of claims 1 to 18, further comprising a compound in which a one-electron-oxidized form generated by an oxidizing of one electron therein can release one or more electrons by a subsequent reaction.

[Claim 20] The photothermographic material of claim 19, wherein the compound in which a one-electron-oxidized form generated by an oxidizing of one electron therein can release one or more electrons by a subsequent reaction is at least a compound selected from the following compounds of types 1 to 5:

(type 1) a compound in which a one-electron-oxidized form generated by oxidizing one electron therein, following a subsequent bond-cleavage reaction, can further release 2 or more electrons;

(type 2) a compound in which a one-electron-oxidized form

generated by oxidizing one electron therein, following a subsequent bond-cleavage reaction, can further release another electron and in which 2 adsorptive groups to silver halide are present in a same molecule;

(type 3) a compound in which a one-electron-oxidized form generated by oxidizing one electron therein, after being subjected to a subsequent bond-forming step, can further release one or more electrons;

(type 4) a compound in which a one-electron-oxidized form generated by oxidizing one electron therein, after being subjected to a subsequent ring-cleavage reaction in a molecule, can further release one or more electrons; and

(type 5) a compound represented by X-Y in which X represents a reducing group, Y represents a dissociating group, and the reducing group represented by X in which a one-electron-oxidized form generated by oxidizing one electron therein, following a subsequent cleavage reaction of an X-Y bond, dissociates Y to generate an X radical from which another electron can further be released.

[Claim 21] The photothermographic material of any one of claims 1 to 20, further comprising a development accelerator.

[Claim 22] The photothermographic material of any one of claims 1 to 21, further comprising a compound having an

adsorptive group to the silver halide and a reducing group.

[Claim 23] The photothermographic material of claim 22, further comprising a compound represented by the following formula (I) as the compound having an adsorptive group and a reducing group:

Formula (I)  $A-(W)_n-B$

wherein A represents a group adsorbable to silver halide (hereinafter referred to simply as "adsorptive group");

W represents a divalent linking group;

n represents 0 or 1; and

B represents a reducing group.

[Claim 24] The photothermographic material of any one of claims 1 to 23, wherein the image-forming layer is provided on each side of the support.

[Claim 25] The photothermographic material of claim 24, imagewise exposed by using an X-ray intensifying screen,

wherein, when exposure is conducted by using a monochromatic light which has a same wavelength as that of a main luminescent peak of the X-ray intensifying screen and a half bandwidth of  $15 \pm 5$  nm, an exposure quantity necessary for an image density, which is obtained by removing an image-forming layer provided on a side opposite to an exposed face from the

support, to become the minimum density plus 0.5 is in a range from 0.005 lux-second to 0.07 lux-second.

[Claim 26] An image forming method using the photothermographic material of claim 24 or 25, the method comprising the steps of:

(a) obtaining an image-forming combined system by providing the photothermographic material between a pair of X-ray intensifying screens;

(b) placing a subject between the combined system and an X-ray source;

(c) irradiating an X-ray having an energy level of from 25 kVp to 125 kVp on the subject;

(d) retrieving the photothermographic material from the combined system; and

(e) heating the thus-retrieved photothermographic material at a temperature of from 90°C to 180°C.

[Claim 27] The photothermographic material of any one of claims 1 to 23, comprising the image-forming layer provided only on one surface of the support, wherein, when exposure is conducted by using an X-ray intensifying screen and a monochromatic light which has a same wavelength as that of a main luminescent peak of the intensifying screen and a half bandwidth of  $15 \pm 5$  nm, an exposure quantity necessary for the



density of an image after thermal development to become the minimum density plus 0.5 is in a range from 0.01 lux-second to 0.07 lux-second, and an image contrast after thermal development is in a range from 3.0 to 5.0.

[Claim 28] An image forming method in which a soft tissue is photographed on the photothermographic material of claim 27 by using an X-ray having a tube potential of no more than 40 kV.

[Claim 29] The photothermographic material of any one of claims 1 to 24 and 27, further comprising an ultraviolet ray-absorbing agent.

[Claim 30] The photothermographic material of claim 29, used in combination with an X-ray intensifying screen having a luminescent peak in an ultraviolet region.

#### [DETAILED DESCRIPTION OF THE INVENTION]

[0001]

#### [Technical Field of the Invention]

The present invention relates to photothermographic materials and image-forming methods and, particularly, to a photothermographic material containing a silver halide emulsion having a high silver iodide content and an image-forming

method using the photothermographic material. More specifically, the present invention relates to a photothermographic material in which sensitivity is substantially improved, fog is low, and storability of images after development is excellent, and an image-forming method using the photothermographic material.

[0002]

[Prior Art]

In recent years, in the fields of medical diagnosis and printing plate forming from the standpoints of environmental protection and space saving, photographic development processing performed in a dry state has been strongly demanded. These fields have seen an increase in digitalization, as well as systems in which image information is fed into a computer and stored and then optionally processed, transmitted, and outputted, by a laser image setter or a laser imager, to a photosensitive material at a position required, and duly developed to form images. Photosensitive materials are now expected to have a capability of being recorded by laser exposure of high illuminance, and a capability to form clear black images having high resolution and sharpness. As for digital imaging recording materials, various types of hard copy systems using pigments and dyes, such as ink jet printers and electronic photographic systems, are available as ordinary image-forming

systems. However, none of these hard copy systems is satisfactory either in terms of aspects of image quality which determine the diagnostic capacity of the images as images for medical uses, such as for example sharpness, graininess, gradation, and color tone, or in respect of the recording speed (i.e. sensitivity of the images), nor have any of these systems yet attained a level of which it can be used to replace the conventional wet-development-type silver salt film used in medical diagnosis.

[0003]

Thermally developable image forming systems utilizing organic silver salts are already known. (See, for example, patent documents 1 and 2, and non-patent document 1.) These systems comprise an image-forming layer in which a reducible silver salt (for example, organic silver salt), a photosensitive silver halide, and, optionally, a color toning agent for controlling the color tone of silver are dispersed in a binder matrix.

[0004]

When the photothermographic material is exposed and heated at a high temperature (for example, 80°C or more), a monochromatic black silver image is produced by an oxidation-reduction reaction between the silver halide, or the reducible silver salt (functioning as an oxidizing agent), and

the reduction agent. The oxidation-reduction reaction is accelerated by catalytic action of a latent image of the silver halide generated by such exposure. Therefore, monochromatic silver images are formed in areas of the material which have been exposed. Such photothermographic materials are disclosed in many documents (see, for example, patent documents 3 and 4) and, further, the Fuji Medical Dry Imager FM-DP L has been commercially available for practical use as an image-forming system for medical diagnosis.

[0005]

However, since such image-forming systems utilizing organic silver salt have no fixing step that allows the silver halide to remain in a layer after thermal development, the systems essentially have two serious drawbacks.

[0006]

One drawback has been image storability after development processing, particularly, printout degeneration caused by exposure to light. A method utilizing silver iodide is known as a means to alleviate printout degeneration. Compared with silver bromide or silver iodobromide having an iodine content of 5 mol% or less, silver iodide has a property which makes it extremely difficult for print out to be generated and in consequence silver iodide has the potential to drastically solve

the problem. However, a silver iodide grain which has been known so far has a sensitivity so low that it is still a long way from being capable of being applied to a practical system. Further, an additional problem inherent in the grain has been that, when, in order to enhance sensitivity, a step has been taken to prevent a reunion of a photon and a hole, a property excellent in printout has thereby been lost.

[0007]

As a method of increasing sensitivity of a silver iodide photographic emulsion, it has been recorded in literature that sensitization can be achieved either by using halogen receptors such as sodium nitrite, pyrogallol, and hydroquinone, by immersion in a silver nitrate aqueous solution, or by sulfur sensitization at pAg 7.5 (see, for example, non-patent documents 2 to 4). However, the sensitizing effects at these halogen receptors on photothermographic materials intended by the present invention has been minimal and conspicuously inadequate.

[0008]

Another drawback is that, because of light scattering caused by residual silver halide, a layer becomes clouded and falls into a state between translucence and opacity, thus causing a deterioration in images. In order to solve this problem,

a practical measure has been adopted in which photosensitive silver halide is made into a state of fine grain (from 0.15  $\mu\text{m}$  to 0.08  $\mu\text{m}$  in an area actually used) and then the quantity of photosensitive silver halide added is reduced as far as possible, thus minimising cloudiness. However, a compromise measure of this kind results in a further decrease in sensitivity and has not completely solved the problem of cloudiness. Opacity has still remained in the layer and haze has remained imparted therein.

[0009]

In the case of a wet development processing system, residual silver halide is removed by performing, after the development process, a process using a fixing liquid containing a silver halide medium. As regards such silver halide media, various types of inorganic and organic compounds which can form a complex with a silver ion are known.

In the case of a dry thermal development process also, incorporation of a similar fixing measure has in the past been attempted. For example, a method has been proposed in which a compound capable of forming a complex with a silver ion is contained in a layer to allow the silver halide to be solubilized by thermal development (ordinarily known as fixing: see patent document 5). However, this method is a system associated with silver bromide or silver chlorobromide, and post-heating is

also necessary for the fixing, requiring, as a heating condition, a temperature as high as from 155°C to 160°C, in which it is difficult to conduct the fixing. Further, another method has been proposed in which a separate sheet (fixing sheet) containing a compound capable of forming a complex with a silver ion is prepared and, then, after the photothermographic material is thermally developed to form an image, the photothermographic material developed is superposed on the fixing sheet and heated to dissolve the remaining silver halide. Thereafter, the silver halide which has been dissolved is removed (see patent document 6). However, since in this method two sheets are used, the treatment process becomes complicated and it has proved difficult to secure operational stability. Further, it is necessary to dispose of the fixing sheet after use in the fixing process. Waste is thereby generated and from a point of view of practicability this becomes a barrier.

[0010]

Further, as for fixing methods in thermal development other than those described above, a method has been proposed in which a fixing agent of a silver halide is first microencapsulated and then the fixing agent is released to act at the time of thermal development (patent document 7). However, for this method, it is difficult to arrive at a design that allows the fixing agent to be effectively released. Still

another method has been proposed in which fixing is performed by using a fixing liquid after thermal development (patent documents 8 and 9). However, in this method a wet-type treatment needs to be performed, and thus this method is not appropriate for a completely dry process.

As described above, there have been known drawbacks to various known methods of improving opacity of the layer that there have invariably been obstacles in the way of putting them to practical use.

[0011]

On the other hand, an attempt has been proposed to apply the aforementioned photothermographic material to a photosensitive material for photographing. The term "photosensitive material for photographing" as used herein does not mean a material in which image information is written by a scanning exposure by means of, for example, laser light, but rather means a material in which an image is recorded by a planar exposure. Since conventionally photothermographic materials have been commonly used in the field of wet development photosensitive materials, a direct or an indirect X-ray film, a mammography film or the like in medical diagnosis applications, various types of plate-making films in printing applications, a recording film in an industrial application, a film for photographing by general-use cameras and the like are all known.



For example, disclosed in patent documents have been a photothermographic material for an X-ray application making use of a blue fluorescent sensitizing paper of a both-sides-coated type (see, for example, patent document 10), a photothermographic material using a tabular grain of silver iodobromide (see, for example, patent document 11), and a photosensitive material for a medical diagnosis application which has a (100) main face and in which a tabular grain having a high silver chloride content is applied on each surface of a support (see, for example, patent document 12). Further, the photothermographic material of a both-sides-coated type has also been disclosed in patent documents other than those described above (see, for example, patent documents 13 to 16). However, in these known examples, when a fine grain silver halide having a size of  $0.1\text{ }\mu\text{m}$  or less is used, haze does not deteriorate, but sensitivity remains low and in consequence the photothermographic material is not able to stand up to practical use. On the other hand, when a silver halide grain having a size of  $0.5\text{ }\mu\text{m}$  or more is used, image quality is severely damaged by a deterioration in haze and printout degradation both caused by residual silver halide, thus preventing the photothermographic material from standing up to practical use.

[0012]

Although a photosensitive material using a tabular grain

of silver iodide as a silver halide grain has been known in the wet development field (see, for example, patent documents 17 and 18), no example is known of a photothermographic material in such applications. The reasons for this are that the photothermographic material has low sensitivity, that no effective sensitizing measures are taken and that, in the case of thermal development, the technical barrier is raised even higher.

[0013]

In order to use the photothermographic material in the application of the photosensitive material for photographing, a higher sensitivity is required and a level of image quality one-step higher than normal is required, with regard both to haze and to other aspects.

[0014]

[Patent Document 1]

USP No. 3,152,904

[Patent Document 2]

USP No. 3,457,075

[Patent Document 3]

USP No. 2,910,377

[Patent Document 4]

Japanese Patent Application Publication (JP-B) No.

43-4924

[Patent Document 5]

Japanese Patent Application Laid-Open (JP-A) No. 8-76317

[Patent Document 6]

JP-A No. 9-166845

[Patent Document 7]

JP-A No. 8-82886

[Patent Document 8]

JP-A No. 51-104826

[Patent Document 9]

JP-A No. 62-133454

[Patent Document 10]

Japanese Patent No. 3,229,344

[Patent Document 11]

JP-A No. 59-142539

[Patent Document 12]

JP-A No. 10-282606

[Patent Document 13]

JP-A No. 2000-227642

[Patent Document 14]

JP-A No. 2001-22027

[Patent Document 15]

JP-A No. 2001-109101

[Patent Document 16]

JP-A No. 2002-90941

[Patent Document 17]

JP-A No. 59-11934

[Patent Document 18]

JP-A No. 59-119350

[Non-Patent Document 1]

D. H. Klosterboer, "Thermally Processed Silver Systems"  
(see *Imaging Processes and Materials, Neblette*, 8th Ed. compiled  
by J. Sturge, V. Walworth and A. Shepp, Chap. 9, page 279, 1989

[Non-Patent Document 2]

*The Journal of Photographic Science*, Vol. 8, p. 119, (1960)

[Non-Patent Document 3]

*The Journal of Photographic Science*, Vol. 28, p. 163,  
(1980)

[Non-Patent Document 4]

*Photographic Science and Engineering*, Vol. 5, page 216  
(1961)

[0015]

[Problems to be Solved by the Invention]

An object of the present invention is to provide a  
photothermographic material using a high silver iodide, and  
an image-forming method using the photothermographic material  
and, particularly, a photothermographic material having a high  
sensitivity, a low fog, and an excellent storability of an image,  
and an image-forming method using the photothermographic

material.

[0016]

[Means for Solving the Problems]

The above-stated object has been attained by measures described below.

(1) A photothermographic material comprising, on a surface of a support, an image-forming layer comprising at least a photosensitive silver halide, a non-photosensitive organic silver salt, a reduction agent for a silver ion, and a binder,

wherein: 1) a silver iodide content in the photosensitive silver halide is in a range from 40 mol% to 100 mol%; and 2) an average sphere-equivalent diameter of the photosensitive silver halide is in a range from 0.3  $\mu\text{m}$  to 5.0  $\mu\text{m}$ .

(2) The photothermographic material of (1), further comprising a compound which after thermal development substantially reduces visible light absorption caused by the photosensitive silver halide.

(3) The photothermographic material of (2), further comprising a silver iodide complex forming agent as the compound which after thermal development substantially reduces visible light absorption caused by the photosensitive silver halide.

[0017]

(4) The photothermographic material of any one of (1) to (3),

wherein the photosensitive silver halide is contained as tabular silver halide grains having an aspect ratio of no less than 2.

(5) The photothermographic material of any one of (1) to (4), wherein at least 50%, in terms of a projected area, of the photosensitive silver halide grains is occupied by tabular grains having an aspect ratio of from 2 to 50.

(6) The photothermographic material of any one of (1) to (5), wherein the average sphere-equivalent diameter of the photosensitive silver halide is in a range from 0.5  $\mu\text{m}$  to 3.0  $\mu\text{m}$ .

(7) The photothermographic material of any one of (1) to (6), wherein the photosensitive silver halide contains silver iodide in an amount from 70 mol% to 100 mol%.

(8) The photothermographic material of any one of (1) to (7), wherein the photosensitive silver halide contains silver iodide in an amount from 80 mol% to 100 mol%.

(9) The photothermographic material of any one of (1) to (8), wherein the photosensitive silver halide contains silver iodide in an amount from 90 mol% to 100 mol%.

(10) The photothermographic material of any one of (1) to (9), wherein the silver iodide complex forming agent is a compound represented by one of the following formulas (1) and (2):

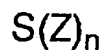
[0018]

[Formula 6]

Formula (1)



Formula (2)



[0019]

wherein, in the formula (1), Y represents a non-metallic atomic group necessary for forming a 5- to 7-membered heterocycle containing at least one of a nitrogen atom and a sulfur atom;

the heterocycle formed by Y may be saturated or unsaturated, or may have a substituent; and

substituents on the heterocycle formed by Y may be combined with each other to form a ring; and

wherein, in the formula (2), Z represents a hydrogen atom or a substituent;

n represents an integer of 1 or 2,

when n represents 1, S and Z are combined with each other by a double bond;

when n represents 2, S and each of two Zs are combined with each other by a single bond;

when n represents 1, Z does not represent a hydrogen atom; and

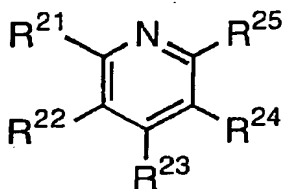
when n represents 2, two Z's may be same as, or different from, each other, but neither of the two Zs represents a hydrogen atom.

(11) The photothermographic material of (10), wherein the compound represented by the formula (1) is a pyridine derivative represented by the following formula (3):

[0020]

Formula (3)

[Formula 7]



[0021]

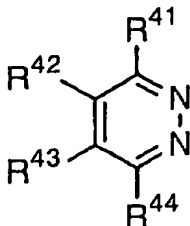
wherein  $R^{21}$  to  $R^{25}$  each independently represent a hydrogen atom or a substituent and may be combined with one another to form a saturated or unsaturated ring.

(12) The photothermographic material of (10), wherein the compound represented by the formula (1) is a pyridazine derivative represented by the following formula (4):

[0022]

Formula (4)

[Formula 8]





[0023]

wherein  $R^{41}$  to  $R^{44}$  each independently represent a hydrogen atom or a substituent and may be combined with one another to form a saturated or unsaturated ring.

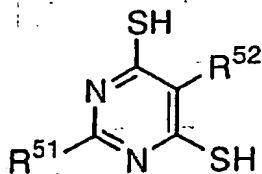
(13) The photothermographic material of (10), wherein the compound represented by the formula (1) is a 5- to 7-membered heterocycle having at least one mercapto group as a substituent and having at least one of a nitrogen atom and a sulfur atom.

(14) The photothermographic material of (10), wherein the compound represented by the formula (1) is a compound represented by one of the following formulas (5) to (7):

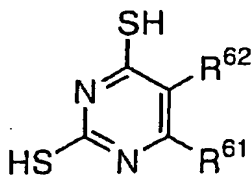
[0024]

[Formula 9]

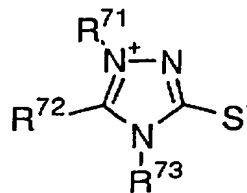
Formula (5)



Formula (6)



Formula (7)



[0025]

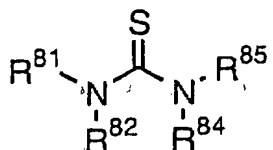
wherein  $R^{51}$  and  $R^{52}$ ,  $R^{61}$  and  $R^{62}$ , and  $R^{71}$  to  $R^{73}$  each independently represent a hydrogen atom or a substituent.

(15) The photothermographic material of (10), wherein the compound represented by the formula (2) is a compound represented by one of the following formulas (8) and (9):

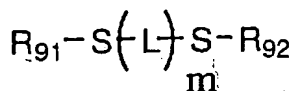
[0026]

[Formula 10]

Formula (8)



Formula (9)



[0027]

wherein  $\text{R}^{81}$  and  $\text{R}^{85}$ , and  $\text{R}^{91}$  to  $\text{R}^{92}$  each independently represent a hydrogen atom or a substituent; L represents a divalent linking group; and m is 0 or 1.

(16) The photothermographic material of any one of (10) to (14), wherein the compound represented by the formula (1) is a nitrogen-containing heterocyclic compound, and an acid dissociation constant (pKa) of a conjugate acid thereof in a tetrahydrofuran/water (3/2) mixed solution at 25°C is preferably in a range from 3 to 8.

(17) The photothermographic material of any one of (10), (11) and (16), wherein the compound represented by the formula (1) is the pyridine derivative represented by the formula (3), and an acid dissociation constant (pKa) of a conjugate acid thereof in a tetrahydrofuran/water (3/2) mixed solution at 25°C is preferably in a range from 3 to 8.

[0028]

(18) The photothermographic material of any one of (1) to (17), further comprising at least one type of phthalic acid or a derivative thereof.

(19) The photothermographic material of any one of (1) to (18), further comprising a compound in which a one-electron-oxidized form generated by an oxidizing of one electron therein can release one or more electrons by a subsequent reaction.

(20) The photothermographic material of (19), wherein the compound in which a one-electron-oxidized form generated by an oxidizing of one electron therein can release one or more electrons by a subsequent reaction is at least a compound selected from the following compounds of types 1 to 5:

(type 1) a compound in which a one-electron-oxidized form generated by oxidizing one electron therein, following a subsequent bond-cleavage reaction, can further release 2 or more electrons;

(type 2) a compound in which a one-electron-oxidized form generated by oxidizing one electron therein, following a subsequent bond-cleavage reaction, can further release another electron and in which 2 adsorptive groups to silver halide are present in a same molecule;

(type 3) a compound in which a one-electron-oxidized form generated by oxidizing one electron therein, after being subjected to a subsequent bond-forming step, can further release

one or more electrons;

(type 4) a compound in which a one-electron-oxidized form generated by oxidizing one electron therein, after being subjected to a subsequent ring-cleavage reaction in a molecule, can further release one or more electrons; and

(type 5) a compound represented by X-Y in which X represents a reducing group, Y represents a dissociating group, and the reducing group represented by X in which a one-electron-oxidized form generated by oxidizing one electron therein, following a subsequent cleavage reaction of an X-Y bond, dissociates Y to generate an X radical from which another electron can further be released.

[0029]

(21) The photothermographic material of any one of (1) to (20), further comprising a development accelerator.

(22) The photothermographic material of any one of (1) to (21), further comprising a compound having an adsorptive group to the silver halide and a reducing group.

(23) The photothermographic material of (22), further comprising a compound represented by the following formula (I) as the compound having an adsorptive group and a reducing group:

Formula (I)  $A - (W)_n - B$

wherein A represents a group adsorbable to silver halide (hereinafter referred to simply as "adsorptive group");

W represents a divalent linking group;

n represents 0 or 1; and

B represents a reducing group.

(24) The photothermographic material of any one of (1) to (23), wherein the image-forming layer is provided on each side of the support.

(25) The photothermographic material of (24), imagewise exposed by using an X-ray intensifying screen,

wherein, when exposure is conducted by using a monochromatic light which has a same wavelength as that of a main luminescent peak of the X-ray intensifying screen and a half bandwidth of  $15 \pm 5$  nm, an exposure quantity necessary for an image density, which is obtained by removing an image-forming layer provided on a side opposite to an exposed face from the support, to become the minimum density plus 0.5 is in a range from 0.005 lux·second to 0.07 lux·second.

[0030]

(26) An image forming method using the photothermographic material of (24) or (25), the method comprising the steps of:

(a) obtaining an image-forming combined system by providing the photothermographic material between a pair of X-ray intensifying screens;

(b) placing a subject between the combined system and an X-ray source;

(c) irradiating an X-ray having an energy level of from 25 kVp to 125 kVp on the subject;

(d) retrieving the photothermographic material from the combined system; and

(e) heating the thus-retrieved photothermographic material at a temperature of from 90°C to 180°C.

[0031]

(27) The photothermographic material of any one of (1) to (23), comprising the image-forming layer provided only on one surface of the support, wherein, when exposure is conducted by using an X-ray intensifying screen and a monochromatic light which has a same wavelength as that of a main luminescent peak of the intensifying screen and a half bandwidth of  $15 \pm 5$  nm, an exposure quantity necessary for the density of an image after thermal development to become the minimum density plus 0.5 is in a range from 0.01 lux·second to 0.07 lux·second, and an image contrast after thermal development is in a range from 3.0 to 5.0.

(28) An image forming method in which a soft tissue is photographed on the photothermographic material of claim 27 by using an X-ray having a tube potential of no more than 40 kV.

(29) The photothermographic material of any one of (1) to (24) and (27), further comprising an ultraviolet ray-absorbing

agent.

(30) The photothermographic material of (29), used in combination with an X-ray intensifying screen having a luminescent peak in an ultraviolet region.

[0032]

[Embodiments]

#### 1. Photothermographic Material

A photothermographic material according to the present invention comprises an image-forming layer comprising a photosensitive silver halide, a non-photosensitive organic silver salt, a reduction agent, and a binder on at least one surface of a support. Further, the photothermographic material according to the invention may preferably comprise a surface protective layer on the image-forming layer, or a back layer or a back protective layer on an opposite surface of the support.

Constitutions of these layers and a preferable constitution thereof will be described in detail below.

[0033]

(Compound Capable of Substantially Reducing Visible Light Absorption Caused by Photosensitive Silver Halide after Thermal Development)

According to the invention, it is preferable to contain a compound which substantially reduces visible light absorption

caused by the photosensitive silver halide after thermal development instead of that before the thermal development.

According to the invention, as for such compounds which substantially reduce the visible light absorption caused by the photosensitive silver halide after thermal development, a silver iodide complex forming agent is particularly preferably used.

[0034]

(Description of Silver Iodide Complex Forming Agent)

The silver iodide complex forming agent according to the invention is capable of contributing to a Lewis acid-base reaction in which at least one of a nitrogen atom and a sulfur atom contained in the compound supplies an electron to a silver ion as a coordination atom (electron donor: Lewis base). Stability of the complex is defined in terms of either a stepwise stability constant or a total stability constant and depends on combinations of 3 factors, namely, a silver ion, an iodine ion, and the silver iodide complex forming agent. As an ordinary indication, a large stability constant can be obtained by a chelate effect caused by intramolecular chelate ring formation, or a measure of, for example, increasing an acid-base dissociation constant of a ligand.

[0035]



Although an action mechanism of the silver iodide complex forming agent according to the invention has not clearly been elucidated, it is considered that silver iodide is allowed to be solubilized by forming a stable complex comprising components of at least 3 elements including an iodine ion and silver ion. Though deficient in capability of solubilizing silver bromide or silver chloride, the silver iodide complex forming agent according to the invention specifically acts on silver iodide.

[0036]

Although a detail of the mechanism in which an image storability is improved by the silver iodide complex forming agent according to the invention is not elucidated, the mechanism is considered as that at least one portion of the photosensitive silver halide and the silver iodide complex forming agent according to the invention are allowed to react with each other at the time of thermal development to form a complex and, accordingly, photosensitivity is reduced or lost, thereby greatly improving the image storability under a light irradiation. At the same time, opacity of a film caused by the silver halide is reduced and, as a result, it is marked characteristics that the image having a high image quality can be obtained. Such reduction of the opacity of the film can be confirmed by measuring the reduction of ultraviolet visible absorption of spectral absorption spectrum.

[0037]

According to the invention, the ultraviolet visible absorption spectrum of the photosensitive silver halide can be measured by a transmittance method or a reflection method. When absorption caused by another compound added to the photothermographic material and absorption caused by the photosensitive silver halide are superimposed, the ultraviolet visible absorption spectrum of the photosensitive silver halide can be observed by using differential spectrum and a measure of, for example, removal of other compounds by a solvent each individually or in combination.

[0038]

It is essential from the standpoint of forming a stable complex by an iodine ion that the silver iodide complex forming agent according to the invention is clearly different from a conventional silver ion complex forming agent. There are marked characteristics in that, contrary to the conventional silver ion complex forming agent which performs a dissolution action on a salt having a silver ion such as silver bromide, silver chloride, or an organic silver salt, for example, silver behenate, the silver iodide complex forming agent according to the invention does not perform such action unless silver iodide is present.

[0039]

Preferable compounds as the silver iodide complex forming agents according to the invention are those represented by the formulas (1) and (2).

In the formula (1), Y represents a non-metallic atomic group necessary for forming a 5- to 7-membered heterocycle having at least one of a nitrogen atom and a sulfur atom. The heterocycle to be formed by Y may be saturated or unsaturated and, also, may have a substituent or may not have a substituent. Such substituents on the heterocycle to be formed by Y may be combined with each other to form a ring.

[0040]

Examples of such 5- to 7-membered heterocycles to be formed by Y each having at least one of a nitrogen atom and a sulfur atom include thiophene, pyrrole, pyridine, oxazole, isooxazole, thiazole, isothiazole, imidazole, pyrazole, pyrazine, pyrimidine, pyridazine, indole, isoindole, indolidine, quinoline, isoquinoline, benzimidazole, 1H-imidazole, quinoxaline, quinazoline, cinnoline, phthalazine, 1,8-naphthyridine, purine, pteridine, carbazole, acrydine, phenanthridine, 1,10-phenathroline, phenazine, phenoxazine, phenothiazine, benzothiazole, benzoxazole, benzimidazole, 1,2,4-triazine, 1,3,5-triazine, pyrrolidine, imidazolidine,

pyrazolidine, piperidine, piperazine, morpholine, indoline, and isoindoline.

[0041]

These rings may each have a substituent; examples of preferable substituents include a halogen atom (a fluorine atom, a chlorine atom, a bromine atom, or an iodine atom), an alkyl group (inclusive of a straight-chain, branched-chain, or cyclic alkyl group inclusive of a bicycloalkyl group and an active methine group), an alkenyl group, an alkynyl group, an aryl group, a heterocyclic group (a position to be substituted is not limited), an acyl group, an alkoxycarbonyl group, an aryloxy carbonyl group, a heterocycloxy carbonyl group, a carbamoyl group, an N-acyl carbamoyl group, an N-sulfonyl carbamoyl group, an N-carbamoyl carbamoyl group, a thiocarbamoyl group, an N-sulfamoyl carbamoyl group, a carbazoyl group, a carboxyl group or a salt thereof, an oxalyl group, an oxamoyl group, a cyano group, a carbonimidoyl group, a formyl group, a hydroxyl group, an alkoxy group (inclusive of a group having a recurring unit of an ethyleneoxy group or a propyleneoxy group), an aryloxy group, a heterocycloxy group, an acyloxy group, an (alkoxy or aryloxy) carbonyloxy group, a carbamoyloxy group, a sulfonyloxy group, an amino group, (an alkyl, aryl, or a heterocycle) amino group, an acylamino group, a sulfonamide group, a ureido group, a thioureido group, an

imido group, an (alkoxy or aryloxy) carbonylamino group, a sufamoylamino group, a semicarbazide group, a thiosemicarbazide group, an ammonio group, an oxamoylamino group, an N-(alkyl or aryl) sulfonylureido group, an N-acylureido group, an N-acylsulfamoylamino group, a nitro group, a heterocyclic group having a quaternized nitrogen atom (for example, a pyridinio group, an imidazolio group, a quinolinio group, or an isoquinolinio group), an isocyano group, an imino group, a mercapto group, (an alkyl, aryl, or a heterocyclo) thio group, (an alkyl, aryl, or a heterocyclo) dithio group, an (alkyl or aryl) sulfonyl group, an (alkyl or aryl) sulfinyl group, a sulfo group or a salt thereof, a sulfamoyl group, an N-acylsulfamoyl group, an N-sulfonylsulfamoyl group or a salt thereof, a phosphino group, a phosphinyl group, a phosphinyloxy group, a phosphinylamino group, and a silyl group. Further, the term "active methine" as used herein is intended to mean a methine group substituted by two electron-attracting groups; the term "electron-attracting group" as used herein is intended to mean an acyl group, an alkoxycarbonyl group, an aryloxy carbonyl group, a carbamoyl group, an alkylsulfonyl group, an arylsulfonyl group, a sufamoyl group, a trifluoromethyl group, a cyano group, a nitro group, or a carbonimidoyl group. Two electron-attracting groups may be combined with each other to form a cyclic configuration. Further, the term "salt" as used herein is intended to mean

a cation of, for example, an alkaline metal, an alkaline earth metal, or a heavy metal, or an organic cation such as an ammonium ion, and a phosphonium ion. The above-described substituents may each further be substituted by any of these substituents. A heterocycle formed by Y may further be condensed with a given ring.

[0042]

Compounds represented by the formula (1) are each preferably a nitrogen-containing heterocyclic compound. An acid dissociation constant (pKa) of a conjugate acid thereof in a tetrahydrofuran/water (3/2) mixed solution at 25°C is preferably in a range from 3 to 8, and more preferably 4 to 7.

The compounds represented by the formula (1) preferably each have a pyridine ring, a pyrimidine ring, or a pyridazine ring (inclusive of a condensed pyridazine such as phthalazine) and, also preferably, each have at least one mercapto group as a substituent. It is particularly preferable that the compounds represented by the formula (1) each have a pyridine ring or a phthalazine ring.

[0043]

In the formula (2), Z represents a hydrogen atom or a substituent. n represents an integer of 1 or 2 and, when n

is 1, S and Z are combined with each other by a double bond, while, when n is 2, S and each of two Z's are combined with each other by a single bond. Further, when n is 1, Z does not represent a hydrogen atom, while, when n is 2, two Z's may be same with or different from each other but none of two Z's represents a hydrogen atom. Still further, it is preferable that Z forms a single bond or a double bond with S by a carbon atom thereof.

When n is 1, examples of Z include methylene, ethylidene, and vinylidene and, further, these groups may each have a substituent; examples of such substituents include the examples of substituents of heterocycles formed by Y in the formula (1). Examples of compounds formed by allowing Z having a substituent to be combined with S include thiourea, tetramethyl thiourea, N-ethyl-N'-propyl thiourea, N,N'-dimethyl thiourea.

When n is 2, examples of substituents represented by Z include an alkyl group (inclusive of a cycloalkyl group such as a bicycloalkyl group), an alkenyl group (inclusive of a cycloalkenyl group such as a bicycloalkenyl group), an alkenyl group, an aryl group, a heterocyclic group, an acyl group, an aryloxycarbonyl group, an alkoxycarbonyl group, a carbamoyl group and an imido group.

[0044]

More particularly mentioned are an alkyl group

(preferably an alkyl group having from 1 to 30 carbon atoms, such as a methyl group, an ethyl group, an n-propyl group, an isopropyl group, a t-butyl group, an n-octyl group, an eicosyl group, a 2-chloroethyl group, a 2-cyanoethyl group or a 2-ethylhexyl group), a cycloalkyl group (preferably a substituted or unsubstituted cycloalkyl group having from 3 to 30 carbon atoms, such as a cyclohexyl group, a cyclopentyl group or a 4-n-dodecylcyclohexyl group), a bicycloalkyl group (preferably a substituted or unsubstituted bicycloalkyl group having from 5 to 30 carbon atoms, such as a bicyclo[1,2,2]heptan-2-yl group or a bicyclo[2,2,2]octane-3-yl group), an alkenyl group (preferably a substituted or unsubstituted alkenyl group having from 2 to 30 carbon atoms, such as a vinyl group, an allyl group, a prenyl group, a geranyl group or an oleyl group), an alkynyl group (preferably a substituted or unsubstituted alkynyl group having from 2 to 30 carbon atoms, such as an ethynyl group, a propargyl group or a trimethylsilylethynyl group), an aryl group (preferably a substituted or unsubstituted aryl group having from 6 to 30 carbon atoms, such as a phenyl group, a p-tolyl group, a naphthyl group, a m-chlorophenyl group or an o-hexadecanoylamino phenyl group); a heterocyclic group (preferably a monovalent group generated by removing one hydrogen atom from a 5- or 6-membered, substituted or unsubstituted, aromatic or non-aromatic heterocyclic compound,



and more preferably a 5- or 6-membered, aromatic heterocyclic group having from 3 to 30 carbon atoms, such as a 2-furyl group, a 2-thienyl group, a 2-pyrimidinyl group or a 2-benzothiazolyl group), an acyl group (preferably a formyl group, a substituted or unsubstituted alkylcarbonyl group having from 2 to 30 carbon atoms, a substituted or unsubstituted arylcarbonyl group having from 7 to 30 carbon atoms or a substituted or unsubstituted heterocyclocarbonyl group having from 4 to 30 carbon atoms combined with a carbonyl group by a carbon atom thereof, such as an acetyl group, a pivaloyl group, a 2-chloroacetyl group, a stearoyl group, a benzoyl group, a p-n-octyloxyphenylcarbonyl group, a 2-pyridylcarbonyl group or a 2-furylcarbonyl group), an aryloxy carbonyl group (preferably a substituted or unsubstituted aryloxy carbonyl group having from 7 to 30 carbon atoms, such as a phenoxycarbonyl group, an o-chlorophenoxycarbonyl group, an m-nitrophenoxycarbonyl group or a p-t-butylphenoxycarbonyl group), an alkoxycarbonyl group (preferably a substituted or unsubstituted alkoxycarbonyl group having from 2 to 30 carbon atoms, such as a methoxycarbonyl group, an ethoxycarbonyl group, a t-butoxycarbonyl group or an n-octadecyloxycarbonyl group), a carbamoyl group (preferably a substituted or unsubstituted carbamoyl group having from 1 to 30 carbon atoms, such as a carbamoyl group, an N-methylcarbamoyl group, an N,N-dimethylcarbamoyl group, an N,N-di-n-octylcarbamoyl group

or an N-(methylsulfonyl)carbamoyl), and an imido group (preferably an N-succinimide group or an N-phthalimide group). Among these substituents, those which have a hydrogen atom may be deprived of the hydrogen atom and, further, substituted. Examples of complex substituents include a hydroxyethoxyethyl group, a hydroxyethylthioethyl group, and dimethylaminocarbonyl group.

[0045]

In the formula (3),  $R^{21}$  to  $R^{25}$  each independently represent a hydrogen atom or a substituent. Examples of such substituents represented by  $R^{21}$  to  $R^{25}$  include the examples of substituents of heterocycles formed by Y in the formula (1). When the compounds represented by the formula (3) each have a substituent, a preferable substitution site of the substituent is any one of  $R^{22}$  to  $R^{24}$ .  $R^{21}$  to  $R^{25}$  may be combined with one another to form a saturated or unsaturated ring.

In the compounds represented by the formula (3), an acid dissociation constant (pKa) thereof at 25°C in a tetrahydrofuran/water (3/2) mixed solution is preferably from 3 to 8, and more preferably 4 to 7.

[0046]

In the formula (4),  $R^{41}$  to  $R^{44}$  each independently represent a hydrogen atom or a substituent.  $R^{41}$  to  $R^{44}$  may be combined

with one another to form a saturated or unsaturated ring. Examples of such substituents represented by  $R^{41}$  to  $R^{44}$  include the examples of substituents of heterocycles formed by Y in the formula (1), and more preferably an alkyl group, an alkenyl group, an alkynyl group, an aryl group, a hydroxyl group, an alkoxy group, an aryloxy group, a heterocycloxy group, and a phthalazine cycle formed by means of benzene condensed ring. When a hydroxyl group is substituted to a carbon atom adjacent to a nitrogen atom in the compound represented by the formula (4), an equilibrium is present between the compound and pyridazinone.

The compound represented by the formula (4) may particularly preferably form a phthalazine ring which may further have a substituent. Examples of preferable substituents of the phthalazine ring include an alkyl group, an alkenyl group, an alkynyl group, an aryl group, a hydroxyl group, an alkoxy group, and an aryloxy group.

[0047]

In the formulas (5) to (7),  $R^{51}$  and  $R^{52}$ ,  $R^{61}$  and  $R^{62}$ , and  $R^{71}$  to  $R^{73}$  each independently represent a hydrogen atom or a substituent. Examples of such substituents represented by  $R^{51}$  and  $R^{52}$ ,  $R^{61}$  and  $R^{62}$ , and  $R^{72}$  include the examples of substituents of heterocycles formed by Y in the formula (1). Examples of substituents represented by  $R^{71}$  and  $R^{72}$  include an alkyl group

(inclusive of a cycloalkyl group, such as a bicycloalkyl group), an alkenyl group (inclusive of a cycloalkenyl group, such as a bicycloalkenyl group), an alkynyl group, an aryl group, and a heterocyclic group.  $R^{51}$  and  $R^{52}$ ,  $R^{61}$  and  $R^{62}$ , and  $R^{71}$  to  $R^{73}$  may, in each combination, be combined with each other or one another to form a saturated or unsaturated ring.

[0048]

In the formulas (8) and (9),  $R^{81}$  to  $R^{85}$ , and  $R^{91}$  and  $R^{92}$  each independently represent a hydrogen atom or a substituent. L represents a divalent linking group. Examples of such substituents represented by  $R^{81}$  to  $R^{85}$ ,  $R^{91}$  and  $R^{92}$  include an alkyl group (inclusive of a cycloalkyl group, such as a bicycloalkyl group), an alkenyl group (inclusive of a cycloalkenyl group, such as a bicycloalkenyl group), an alkynyl group, an aryl group, a heterocyclic group, an acyl group, an aryloxy carbonyl group, an alkoxy carbonyl group, a carbamoyl group, and an imido group.

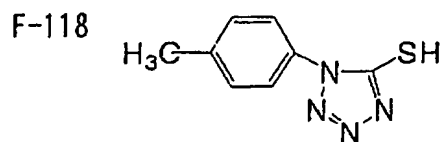
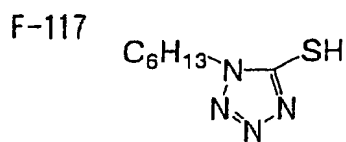
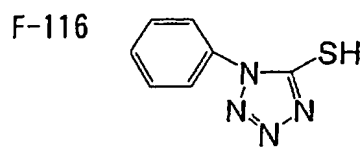
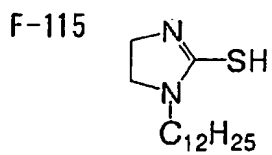
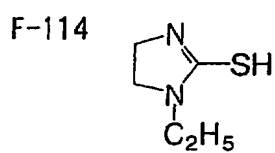
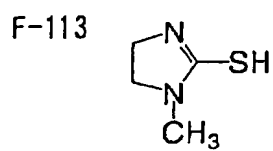
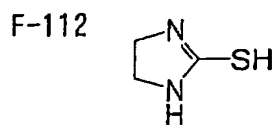
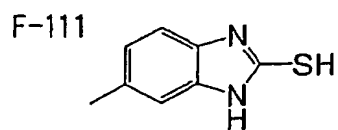
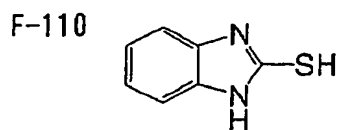
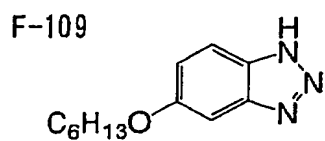
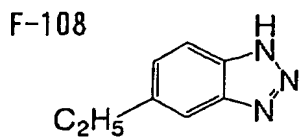
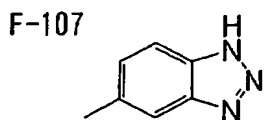
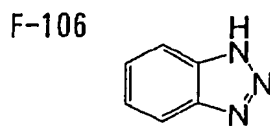
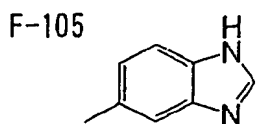
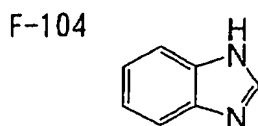
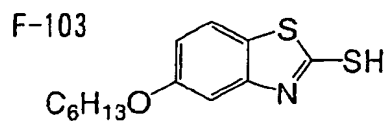
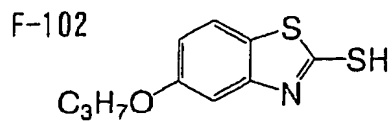
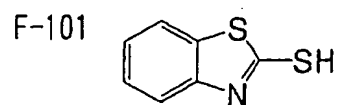
The divalent linking group represented by L is a group which has, preferably, a length corresponding to from 1 to 6 atoms, and more preferably a length corresponding to from 1 to 3 atoms and, further, may have a substituent. Preferable examples of such substituents include  $-\text{CH}_2-$ ,  $-\text{CH}_2\text{CH}_2-$ ,  $-\text{CH}(\text{CH}_3)-$ ,  $-\text{CH}(\text{OH})\text{CH}_2-$ , and  $-\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_2-$ . m represents 0 or 1.

[0049]

Preferable examples of the compounds represented by the formulas (1) and (2) are described below; however, the invention is by no means limited thereto.

[0050]

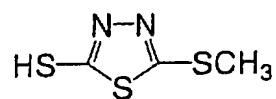
[Formula 11]



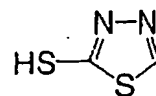
[0051]

[Formula 12]

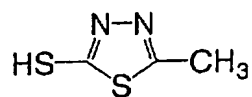
F-119



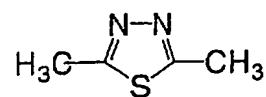
F-120



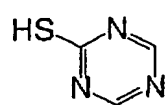
F-121



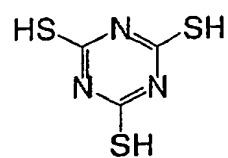
F-122



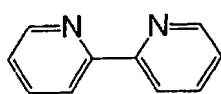
F-123



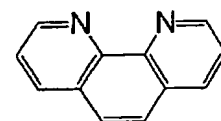
F-124



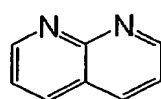
F-125



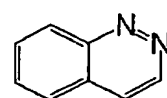
F-126



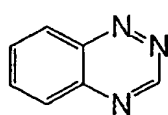
F-127



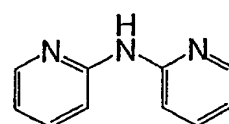
F-128



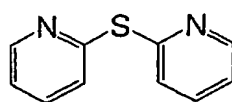
F-129



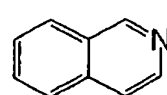
F-130



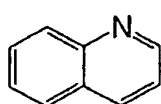
F-131



F-132

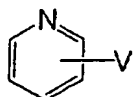


F-133



[0052]

[Formula 13]

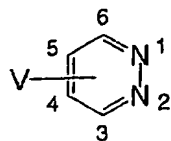


Compound	V
F-301	H
F-302	4-methyl
F-303	4-ethyl
F-304	4-propyl
F-305	2-methyl
F-306	2,6-dimethyl
F-307	3,4-dimethyl
F-308	2,4-dimethyl
F-309	3,5-dimethyl
F-310	2,4,6-trimethyl
F-311	4-phenyl
F-312	4-benzyl
F-313	4-phenethyl
F-314	4-methoxy
F-315	4-benzyloxy
F-316	4-phenoxy
F-317	4-(4-chlorophenyl)oxy
F-318	4-(4-chlorobenzyl)oxy
F-319	4-(4-methylbenzyl)oxy
F-320	4-(4-methoxybenzyl)oxy
F-321	4-amino
F-322	4-dimethylamino
F-323	2-dimethylamino
F-324	4-acetylamino
F-325	4-benzoylamino
F-326	4-(4-pyridyl)
F-327	4-phenoxycarbonyl

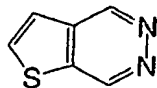


[0053]

[Formula 14]

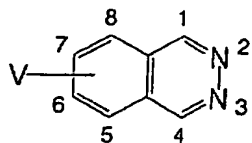


Compound	V
F-401	H
F-402	4-methyl
F-403	4,5-dimethyl
F-404	3,4,5,6-tetramethyl
F-405	4-phenyl
F-406	4-nitro
F-407	4-chloro
F-408	4-amino
F-409	4-benzoylamino
F-410	4-acetylamino
F-411	4-hydroxyl
F-412	4-methoxy
F-413	4,5-dimethoxy
F-414	3-hydroxy
F-415	3-chloro
F-416	3-methyl
F-417	3-methoxy
F-418	3,6-dihydroxy
F-419	4-dimethylamino
F-420	4-acetyl
F-421	



[0054]

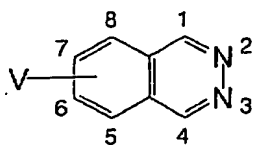
[Formula 15]



Compound	V
F-431	H
F-432	1-phenyl
F-433	1-(4-isopropylphenyl)
F-434	5-methyl
F-435	6-methyl
F-436	5,7-dimethyl
F-437	6,7-dimethyl
F-438	5,6,8-trimethyl
F-439	6-ethyl
F-440	6-isopropyl
F-441	6-isobutyl
F-442	6-propyl
F-443	6-t-butyl
F-444	6-sec-butyl
F-445	6-cyclohexyl
F-446	6-phenyl
F-447	6-benzyl
F-448	6-thienyl
F-449	6-chloro
F-450	6-bromo
F-451	6,7-dichloro
F-452	5,6,7,8-tetrachloro
F-453	1-chloro
F-454	1-methyl
F-455	6-acetyl

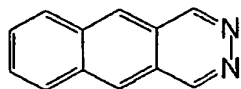
[0055]

[Formula 16]

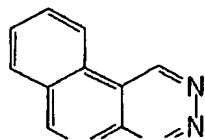


Compound	V
F-456	6-benzoyl
F-457	6-carboxy
F-458	6-methoxycarbonyl
F-459	6-sulfo
F-460	6-hydroxy
F-461	6,7-dihydroxy
F-462	6-methoxy
F-463	6,7-dimethoxy
F-464	6,7-methylenedioxy
F-465	6-acetoxy
F-466	5-nitro
F-467	6-nitro
F-468	5-amino
F-469	6-amino
F-470	5-dimethylamino
F-471	6-dimethylamino
F-472	4-(4-isopropylphenyl)-6-isopropyl
F-473	4-(4-methylphenyl)-6-methyl
F-474	1,4-dicarboxy
F-475	1,4-dichloro
F-476	1,4-di(methoxycarbonyl)
F-477	1,4-dimethyl

F-478

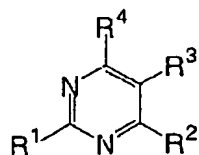


F-479



[0056]

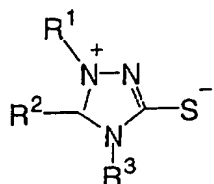
[Formula 17]



Compound	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>
F-501	SH	SH	H	H
F-502	SH	SH	H	OH
F-503	SH	SH	H	SH
F-504	SH	SH	H	CO <sub>2</sub> H
F-505	SH	SH	NH <sub>2</sub>	CH <sub>3</sub>
F-506	SH	SH	H	CH <sub>2</sub> CO <sub>2</sub> CH <sub>3</sub>
F-507	SH	SH	H	NCH <sub>3</sub> (CH <sub>2</sub> CO <sub>2</sub> H)
F-508	NCH <sub>3</sub> (CH <sub>2</sub> CO <sub>2</sub> H)	SH	H	SH
F-509	NCH <sub>3</sub> (CH <sub>2</sub> CO <sub>2</sub> Na)	SH	H	SH
F-510	SH	SH	H	NCH <sub>3</sub> (CH <sub>2</sub> CO <sub>2</sub> H)
F-511	SH	SH	H	NH(CH <sub>2</sub> ) <sub>2</sub> CO <sub>2</sub> H
F-512	SH	SH	H	CONHCH <sub>2</sub> CO <sub>2</sub> H
F-513	SH	SH	H	CON(CH <sub>3</sub> )CH <sub>2</sub> CO <sub>2</sub> H
F-514	SH	SH	H	N(CH <sub>3</sub> )CH <sub>2</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>
F-515	SH	SH	H	NHC <sub>6</sub> H <sub>5</sub>
F-516	SH	SH	H	
F-517	SH	SH	H	
F-518	SH	SH	H	-OC <sub>6</sub> H <sub>13</sub>
F-519	SH	SH	H	-N(CH <sub>2</sub> CO <sub>2</sub> H) <sub>2</sub>
F-520	SH	SH	H	-N(CH <sub>2</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>
F-521	SH	SH	H	CONH(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>
F-522	SH	SH	H	CH <sub>2</sub> CO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>
F-523	SH	SH	H	CH <sub>2</sub> -
F-524	SH	SH	H	N(CH <sub>3</sub> )CH <sub>2</sub> CH <sub>2</sub> SO <sub>3</sub> Na

[0057]

[Formula 18]

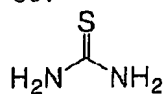


Compound	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>
F-701	CH <sub>3</sub>	H	C <sub>2</sub> H <sub>5</sub>
F-702	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>
F-703	CH <sub>3</sub>	H	C <sub>3</sub> H <sub>7</sub>
F-704	CH <sub>3</sub>	CH <sub>3</sub>	i-C <sub>3</sub> H <sub>7</sub>
F-705	CH <sub>3</sub>	H	C <sub>4</sub> H <sub>9</sub>
F-706	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>2</sub> SO <sub>3</sub> H
F-707	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>2</sub> CO <sub>2</sub> H
F-708	CH <sub>3</sub>	CH <sub>3</sub>	NHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>
F-709	CH <sub>3</sub>	CH <sub>3</sub>	NHCO <sub>2</sub> C <sub>6</sub> H <sub>13</sub>
F-710	CH <sub>3</sub>	CH <sub>3</sub>	C <sub>12</sub> H <sub>25</sub>
F-711	CH <sub>3</sub>	CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> CH <sub>3</sub>	CH <sub>3</sub>
F-712	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	CH <sub>3</sub>
F-713	C <sub>6</sub> H <sub>5</sub>	H	CH <sub>3</sub>
F-714	t-C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	CH <sub>3</sub>
F-715	i-C <sub>3</sub> H <sub>7</sub>	CH <sub>3</sub>	CH <sub>3</sub>
F-716	t-C <sub>4</sub> H <sub>9</sub>	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>
F-717	t-C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>
F-718	CH <sub>3</sub>	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>
F-719	CH <sub>3</sub>	H	C <sub>6</sub> H <sub>13</sub>
F-720	CH <sub>3</sub>	H	C <sub>6</sub> H <sub>13</sub>

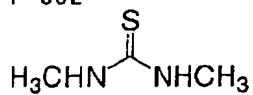
[0058]

[Formula 19]

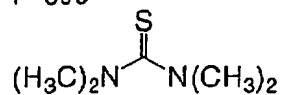
F-801



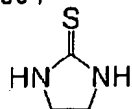
F-802



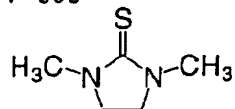
F-803



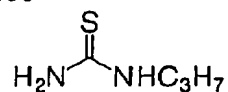
F-804



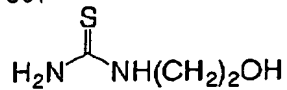
F-805



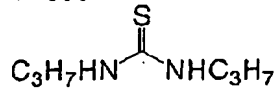
F-806



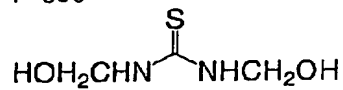
F-807



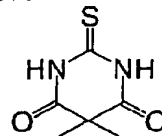
F-808



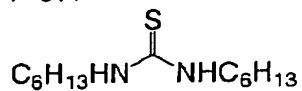
F-809



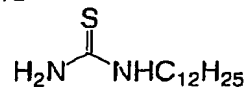
F-810



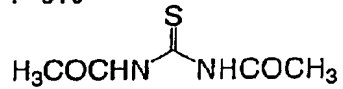
F-811



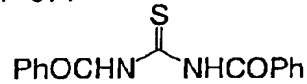
F-812



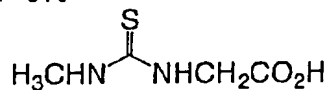
F-813



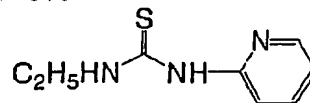
F-814



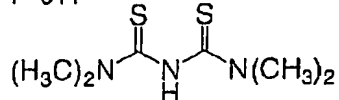
F-815



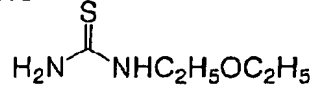
F-816



F-817

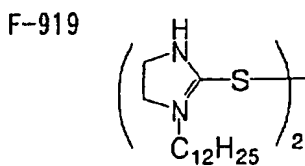
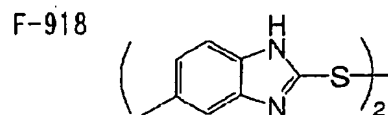
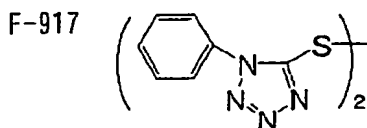
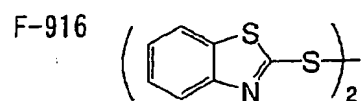
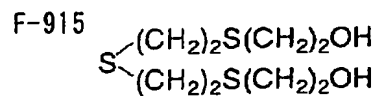
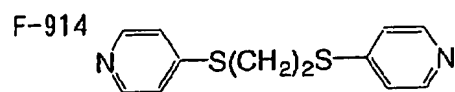
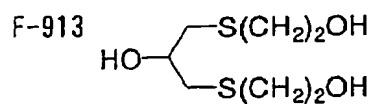
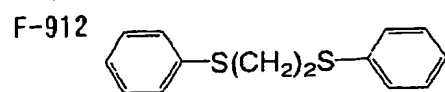
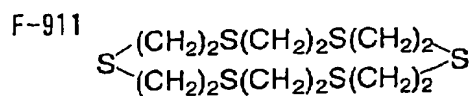
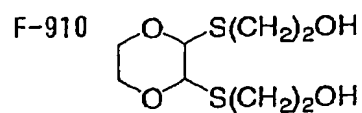
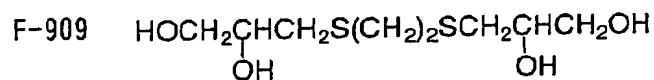
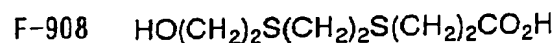
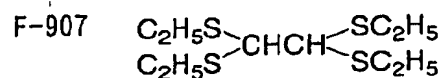
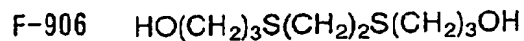
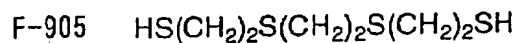
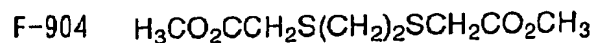
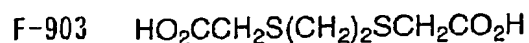
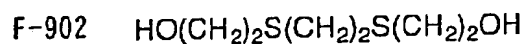
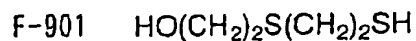


F-818



[0059]

[Formula 20]



[0060]

When the silver iodide complex forming agent according to the invention performs a function of a color toning agent which has been known, the silver iodide complex forming agent and the color toning agent can be of a common compound. When the silver iodide complex forming agent according to the invention does not perform a function of a color toning agent which has been known, the silver iodide complex forming agent can simultaneously be used with the color toning agent. For example, a compound known as a color toning agent is present in pyridazine derivatives (for example, phthalazine) represented by the formula (4) according to the invention. However, although it has been known that the phthalazine compound is effective as a color toning agent in the photothermographic material, it has not been known at all that the phthalazine compound has a function of the silver iodide complex forming agent according to the invention. Further, since there was no understanding of the compound itself which has the function of the silver iodide complex forming agent, the function thereof has also not been expected. When the phthalazine compound is used as a color toning agent, the phthalazine compound may be used individually or in combination with a different phthalazine derivative.

[0061]



In order to allow the silver iodide complex forming agent according to the invention to effectively act without giving any detrimental effect on storage stability of an unexposed photothermographic material according to the invention and, also, without hindering an image forming reaction, it is desirable that the silver iodide complex forming agent does not act on the photosensitive silver halide before it is heated to be thermally developed and, also, it starts to act in a step in which no substantial effect to thermal development has not yet been generated after it is heated. For this account, it is preferable that the silver iodide complex forming agent according to the invention is allowed to be present in a film in a separated state from the photosensitive silver halide, for example, in a solid state. It is also preferable that the silver iodide complex forming agent is added to an adjacent layer. It is preferable that the silver iodide complex forming agent according to the invention is used in combination with a compound which is in a solid state below room temperature and has an appropriate range of melting point such that it melts when heated at a thermally developing temperature, or a measure for adjusting a melting point by mixing a melting point adjusting agent.

[0062]

According to the invention, in order to substantially

improve image storability, particularly, that under light irradiation, absorption intensity of the ultraviolet visible absorption spectrum of the photosensitive silver halide after thermal development, based on that before thermal development, is preferably 80% or less, more preferably 40% or less, still more preferably 20% or less, and most preferably 10% or less.

[0063]

The silver iodide complex forming agent according to the invention may be contained in a coating solution in any form of solution form, emulsify-dispersion form, solid fine grain dispersion form and the like and the resultant coating solution may be contained in the photosensitive material.

As for well known emulsify-dispersion methods, mentioned is a method in which the silver iodide complex forming agent is dissolved by using an auxiliary solvent such as dibutyl phthalate, tricresyl phosphate, glyceryl triacetate, an oil (for example, diethyl phthalate), ethyl acetate, and cyclohexanone and, then, the resultant solution was mechanically treated to prepare an emulsify-dispersion.

[0064]

Further, as for solid fine grain dispersion methods, mentioned is a method in which the silver iodide complex forming agent according to the invention in powder form is dispersed

in an appropriate solvent such as water by using a ball mill, a colloid mill, a vibration ball mill, a sand mill, a jet mill, a roller mill or an ultrasonic wave to prepare a solid dispersion. On this occasion, any one of a protective colloid (for example, polyvinyl alcohol), and a surfactant (for example, an anionic surfactant such as sodium triisopropyl naphthalene sulfonate (mixture of different types of sulfonates in which substitution sites of 3 isopropyl groups are different from one another)) may be used. In the above-described mills, beads of, for example, zirconia are ordinarily used and there is a chance in which Zr or the like is eluted from the beads into the dispersion. Depending on dispersion conditions, such elution is in a range from 1 ppm to 1000 ppm. However, this elution puts forth no practical problem so long as a Zr content in the photosensitive material is, based on 1 g of silver, 0.5 mg or less.

An antiseptic agent (for example, a sodium salt of benzisothiazolinone) is allowed to be contained in an aqueous dispersion.

The silver iodide complex forming agent according to the invention is preferably used in a state of solid dispersion.

[0065]

The silver iodide complex forming agent according to the invention is used, based on the photosensitive silver halide, preferably in a range from 1 mol% to 5000 mol%, more preferably

from 10 mol% to 1000 mol%, and still more preferably from 50 mol% to 300 mol%.

[0066]

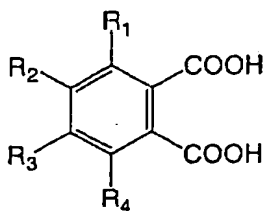
(Phthalic Acid and Derivative Thereof)

According to the invention, not only a silver iodide complex forming agent, but also a compound selected from phthalic acid and the derivatives thereof are preferably contained. As for phthalic acid and the derivatives thereof according to the invention, preferable are compounds represented by the following formula (PH):

[0067]

[Formula 21]

Formula (PH)



[0068]

In the formula (PH), T represents a halogen atom (a fluorine atom, a bromine atom, or an iodine atom), an alkyl group, an aryl group, an alkoxy group, or a nitro group. k represents an integer of 0 to 4. Plural ks may be the same or different from each other when k is 2 or more. k is preferably 0 to 2,

and more preferably 0 or 1.

[0069]

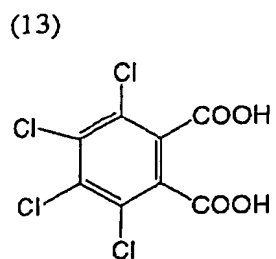
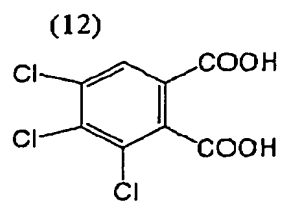
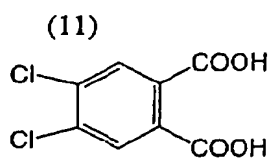
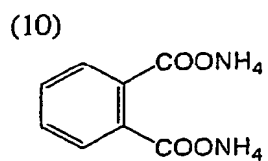
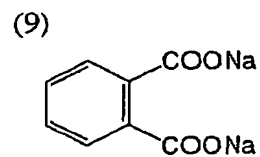
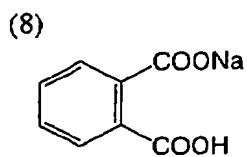
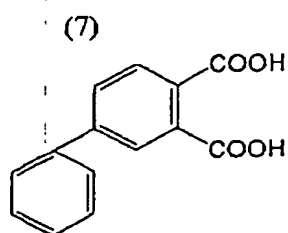
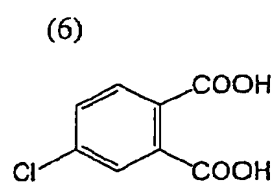
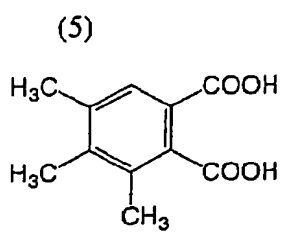
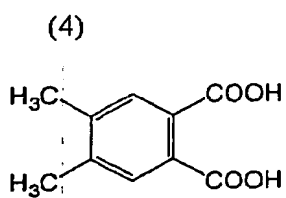
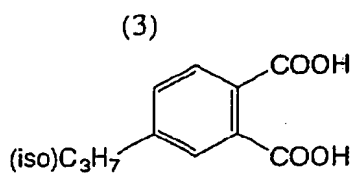
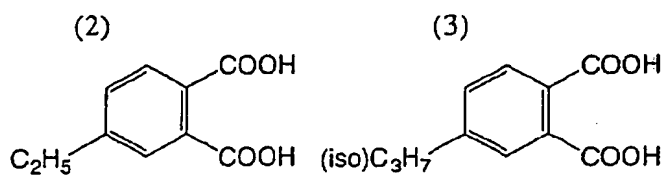
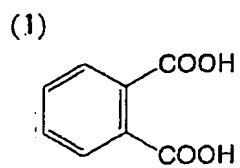
The compounds represented by the formula (PH) may be used in acid form as they are, or in appropriate salt form from the standpoint of easiness of addition to a coating solution, and adjustment of pH. As for salts thereof, an alkaline metal salt, an ammonium salt, an alkaline earth metal salt, an amine salt and the like can be used; an alkaline metal salt (Li, Na, K or the like), and an ammonium salt are preferable thereamong.

[0070]

Specific examples of phthalic acid, and the derivatives thereof according to the invention are described below; however, the invention is by no means limited thereto.

[0071]

[Formula 22]



[0072]

Phthalic acid and the derivatives thereof according to the invention are used, based on 1 mol of silver to be coated, in a range from  $1.0 \times 10^{-4}$  mol to 1 mol, preferably from  $1.0 \times 10^{-3}$  to 0.5 mol, and more preferably from  $2.0 \times 10^{-3}$  mol to 0.2 mol.

[0073]

(Description of Photosensitive Silver Halide)

1) Halogen Composition

It is important that a photosensitive silver halide according to the invention has a composition in which a silver iodide content is as high as 40 mol% to 100 mol%. As a silver halide composition, a remaining component is not particularly limited and can be selected from silver chloride, silver bromide, and organic silver salts such as silver thiocyanate and silver phosphate, in which particularly silver bromide or silver chloride is preferable. By using the silver halide having a composition in which the silver iodide content is high as described above, a favorable photothermographic material in which image storability after subjected to a development process is enhanced, particularly in a point that an increase of fogging to be caused by light irradiation is remarkably small can be designed.

[0074]

Further, the silver iodide content is preferably in a range from 70 mol% to 100 mol%, more preferably from 80 mol% to 100 mol% and particularly preferably from 90 mol% to 100 mol% from the standpoint of the image storability against light irradiation after the development process.

[0075]

Distribution of a halogen composition within a grain may be uniform, changed stepwise, or changed continuously. Further, a silver halide grain having a core/shell structure can also favorably be used. As for structures, a 2- to 5-fold structure is preferably used, and a core/shell grain having a 2- to 4-fold structure can more preferably be used. Still further, a core high silver iodide structure in which a silver iodide content in a core portion is high, or a shell high silver iodide structure in which a silver iodide content in a shell portion is high can also be favorably used. Furthermore, a technique for epitaxially localizing silver chloride or silver bromide on the surface of the grain may also be favorably used.

[0076]

Silver iodide according to the invention may have a given  $\beta$ -phase or  $\gamma$ -phase content. The term " $\beta$ -phase" as used herein is intended to denote a high silver iodide structure having



a hexagonal wurtzite structure while the term " $\gamma$ -phase" as used herein is intended to denote a high silver iodide structure having a cubic zincblend structure. The  $\gamma$ -phase content can be determined by using a technique proposed by C. R. Berry. The technique performs such determination based on peak ratios between any one of silver halide  $\beta$ -phase (100), (101), and (002) faces and silver halide  $\gamma$ -phase (111) face and details of the technique can be referred to *Physical Review*, Vol. 161, No. 3, pp. 848 to 851 (1967).

[0077]

## 2) Grain Size

As far as the silver halide of high silver iodide according to the invention is concerned, a grain size which is large enough for attaining a high sensitivity can be selected. According to the invention, an average sphere-equivalent diameter of the silver halide is preferably in a range from 0.3  $\mu\text{m}$  to 5.0  $\mu\text{m}$  and, more preferably from 0.5  $\mu\text{m}$  to 3.0  $\mu\text{m}$ . The term "sphere-equivalent diameter" as used herein is intended to mean a diameter of a sphere having a same volume as that of one silver halide grain. In regard to a measuring method, the sphere-equivalent diameter can be determined by first obtaining a grain volume based on a projected area and thickness of each grain observed by an electron microscope and, then, converting the form of the grain into a sphere having a same volume as

the thus-obtained volume.

[0078]

### 3) Applied Quantity

Ordinarily, in a case of the photothermographic material in which the silver halide remains after thermal development, when a quantity of the silver halide to be applied is increased, transparency of a film is reduced to deteriorate an image quality. Since this situation is not favorable, sensitivity is forced to be low regardless of a request for enhancing the sensitivity. However, in a case of the invention, since haze of the film to be caused by the silver halide can be reduced by performing a thermally development process, the silver halide can be applied in more quantity than in a conventional case. According to the invention, a quantity of the silver halide grain to be applied is, based on 1 mol of silver of a non-photosensitive organic silver salt, in a range from 0.5 mol% to 100 mol% and preferably from 5 mol% to 50 mol%.

[0079]

### 4) Grain-Forming Method

A method for forming a photosensitive silver halide is well known in the art; for example, methods as described in *Research Disclosure* No. 17029 (June, 1978) and USP No. 3,700,458 can be used and, specifically, a method in which firstly a

photosensitive silver halide is prepared by adding a silver-supplying compound and a halogen-supplying compound to gelatin or at least one of other polymer solutions and, then, the thus-prepared photosensitive silver halide is added with an organic silver salt is used. Further, a method as described in paragraphs [0217] to [0224] of JP-A No. 11-119374, or methods as described in JP-A No. 11-352627 and Japanese Patent Application No. 2000-42336 are preferably used.

As for methods for forming tabular grains of silver iodide, methods as described in JP-A Nos. 59-119350 and 59-119344 are preferably used.

[0080]

#### 5) Grain Form

Examples of forms of silver halide grains according to the invention include a cubic form, an octahedral form, a tetradecehedral form, a dodecahedral form, a tabular form, a spherical form, a rod-like form, and a potato-like form. Particularly, the silver halide grain is preferably dodecahedral, tetradecehedral, and tabular. The term "dodecahedral grain" as used herein is intended to denote a grain having  $\{001\}$ ,  $\{1(-1)0\}$ , and  $\{101\}$  faces, while the term "tetradecehedral grain" as used herein is intended to denote a grain having  $\{001\}$ ,  $\{100\}$  and  $\{101\}$  faces, in which  $\{100\}$  and  $\{101\}$  faces represent a crystalline face group having

equivalent face indices to those of (100) and (101) faces, respectively.

The dodecahedral, tetradecahedral, and octahedral forms of silver iodide can be prepared with reference to Japanese Patent Application Nos. 2002-81020, 2002-87955, and 2002-91756.

In the grain in tabular form, an aspect ratio is 2 or more, and more preferably in a range from 2 to 50.

[0081]

The silver halide having a composition in which a silver iodide content is high according to the invention can take a complicated form; however, examples of preferable forms thereof include a joint grain as described in R. L. Jenkins et al., *The Journal of Photographic Science*, Vol. 28, p. 164, Fig. 1 (1980). Further, a grain in tabular form as shown in *ibid.*, Fig. 1, can also preferably be used. The silver halide grain having a round corner can also be preferably used. There is no particular restriction on a face index (Miller index) of an outer surface of the photosensitive silver halide grain; however, a proportion of [100] face, which is high in spectral sensitization efficiency when a spectral sensitizing dye is adsorbed thereon, is preferably high. The proportion is preferably 50% or more, more preferably 65% or more, and still more preferably 80% or more. The proportion of Miller index

[100] face can be determined by using a method, as described in T. Tani, J. Imaging Sci., 29, 165 (1985), which utilizes adsorption dependency of [111] face and [100] face when a sensitizing dye is adsorbed.

[0082]

#### 6) Heavy Metal

The photosensitive silver halide grain according to the invention can contain a metal belonging to groups 8 to 10 in the periodic table (displaying groups 1 to 18) or a complex thereof. The metal or a center metal of the metal complex belonging to groups 8 to 10 of the periodic table is preferably rhodium, ruthenium, or iridium. One type of these metal complexes may be used or, otherwise, 2 or more types of complexes of same or different metals may simultaneously be used. A content thereof is preferably in the range, based on 1 mol of silver, of from  $1 \times 10^{-9}$  mol to  $1 \times 10^{-3}$  mole. Such heavy metals and metal complexes and, also, addition methods thereof are described in JP-A No. 7-225449, paragraphs [0018] to [0024] of JP-A No. 11-65021, and paragraphs [0227] to [0240] of JP-A No. 11-119374.

[0083]

According to the invention, the silver halide grain which allows a hexacyano metal complex to be present on an outermost

surface thereof is preferable. Examples of such hexacyano metal complexes include  $[\text{Fe}(\text{CN})_6]^{4-}$ ,  $[\text{Fe}(\text{CN})_6]^{3-}$ ,  $[\text{Ru}(\text{CN})_6]^{4-}$ ,  $[\text{Os}(\text{CN})_6]^{4-}$ ,  $[\text{Co}(\text{CN})_6]^{3-}$ ,  $[\text{Rh}(\text{CN})_6]^{3-}$ ,  $[\text{Ir}(\text{CN})_6]^{3-}$ ,  $[\text{Cr}(\text{CN})_6]^{3-}$ , and  $[\text{Re}(\text{CN})_6]^{3-}$ . According to the invention, a hexacyano Fe complex is preferable.

[0084]

Although a counter cation of the hexacyano metal complex is not important because the hexacyano metal complex exists in ionic form in an aqueous solution, it is preferable to use an alkaline metal ion such as a sodium ion, a potassium ion, a rubidium ion, a cesium ion or a lithium ion; an ammonium ion; or an alkyl ammonium ion (for example, a tetramethyl ammonium ion, a tetraethyl ammonium ion, a tetrapropyl ammonium ion or a tetra (n-butyl) ammonium ion), which are each individually easily compatible with water and appropriate for a precipitation operation of a silver halide emulsion.

[0085]

The hexacyano metal complex can be mixed with water, a mixed solvent of water and an appropriate organic solvent compatible with water (for example, alcohols, ethers, glycols, ketones, esters, and amides), or gelatin and, then, added.

[0086]

A quantity of the hexacyano metal complex to be added is, based on 1 mol of silver, preferably in a range from  $1 \times 10^{-5}$  mol to  $1 \times 10^{-2}$  mol, and more preferably from  $1 \times 10^{-4}$  mol to  $1 \times 10^{-3}$  mol.

[0087]

In order to allow the hexacyano metal complex to be present on the outermost surface of the silver halide grain, the hexacyano metal complex is directly added in any stage of: before a loading step which is from completion of an addition of an aqueous silver nitrate solution to be used for grain formation to before a chemical sensitization step in which chalcogen sensitization such as sulfur sensitization, selenium sensitization or tellurium sensitization, or precious metal sensitization such as gold sensitization is performed; during a washing step; during a dispersion step; and before the chemical sensitization step is performed. To inhibit the growth of the silver halide grain, the hexacyano metal complex is preferably added immediately after the grain is formed and, accordingly, preferably before the loading step is completed.

[0088]

Further, an addition of the hexacyano metal complex may be started after 96% by mass of an entire quantity of silver nitrate to be added for the grain formation is added, preferably

started after 98% by mass thereof is added, and particularly preferably started after 99% by mass thereof is added.

When any of these hexacyano metal complexes is added during a period of time between after an addition of the aqueous silver nitrate solution is performed and immediately before grain formation is completed, the hexacyano metal complex can be adsorbed on the outermost surface of the silver halide grain and most of such hexacyano metal complexes each form an insoluble salt with a silver ion on a grain surface. Since a silver salt of hexacyano iron (II) is a more insoluble salt than AgI, it can prevent redissolving to be caused by fine grains; as a result, it has become possible to manufacture a silver halide fine grain having a small grain size.

[0089]

Other metal atoms (for example,  $[\text{Fe}(\text{CN})_6]^{4-}$ ) capable of being contained in the silver halide grain according to the invention, a desalination method and a chemical sensitization method of the silver halide emulsion are described in paragraphs [0046] to [0050] of JP-A No. 11-84574, paragraphs [0025] to [0031] of JP-A No. 11-65021, and paragraphs [0242] to [0250] of JP-A No. 11-119374.

[0090]

7) Gelatin



Various types of gelatin can be used as gelatin to be contained in the photosensitive silver halide emulsion according to the invention. In order to maintain a favorable dispersion state of the photosensitive silver halide emulsion in a coating solution containing an organic silver salt, it is preferable to use low molecular weight gelatin having a molecular weight in a range from 500 to 60,000. These types of gelatin may be used at the time of grain formation or at the time of dispersion after a desalting treatment is performed; however, they are preferably used at the time of dispersion after the desalting treatment is performed.

[0091]

#### 8) Chemical Sensitization

The photosensitive silver halide according to the invention may chemically be unsensitized; however, the photosensitive silver halide according to the invention is preferably chemically sensitized by at least one method of chalcogen sensitization method, a gold sensitization method, and a reduction sensitization method. As for such chalcogen sensitization methods, mentioned are a sulfur sensitization method, a selenium sensitization method and a tellurium sensitization method.

[0092]

In the sulfur sensitization method, an unstable sulfur compound is used; examples of such unstable sulfur compounds capable of being used include those as described, for example, in P. Grafkides, *Chimie et Physique Photographique*, 5th ed., Paul Momtel, (1987), and Research Disclosure, Vol. 307, No. 307105.

Specifically, known sulfur compounds such as thiosulfates (for example, hyposulfite), thioureas (for example, diphenyl thiourea, triethyl thiourea, N-ethyl-N'-(4-methyl-2-thiazolyl)thiourea, and carboxymethyl trimethyl thiourea), thioamides (for example, thioacetamide), rhodanines (for example, diethyl rhodanine, 5-benzylidene-N-ethyl rhodanine), phosphine sulfides (for example, trimethyl phosphine sulfide), thiohydantoins, 4-oxo-oxazolidine-2-thiones, disulfides or polysulfides (for example, dimorpholine disulfide, cystine, and lenthionine (1,2,3,5,6-pentathiepane)), polythionates, elemental sulfur and, active gelatin and the like can be used. Particularly, the thiosulfates, the thioureas, and the rhodanines are preferable.

[0093]

In the selenium sensitization, an unstable selenium compound is used. Examples of such selenium compounds capable of being used include those as described, for example, in JP-B

Nos. 43-13489, and 44-15748, JP-A Nos. 4-25832, 4-109340, 4-271341, 5-40324, and 5-11385, Japanese Patent Application Nos. 4-202415, 4-330495, 4-333030, 5-4203, 5-4204, 5-106977, 5-236538, 5-241642, and 5-286916.

[0094]

Specifically, colloidal metal selenium, selenoureas (for example, N,N-dimethyl selenourea, trifluoromethyl carbonyl-trimethyl selenourea, and acetyl-trimethyl selenourea), selenamides (for example, selenamide, and N,N-diethylphenyl selenamide), phosphine selenides (for example, triphenyl phosphine selenide, and pentafluorophenyl-triphenyl phosphine selenide), selenophosphates (for example, tri-p-tolylselenophosphate, and tri-n-butylselenophosphate), selenoketones (for example, selenobenzophenone), isoselenocyanates, selenocarboxylates, selenoesters, diacyl selenides and the like may be used. Further, non-unstable selenium compounds (for example, selenious acid, selenocyanates, selenazoles and selenides) as described in JP-B Nos. 46-4553, 52-34492 and the like can also be used and, particularly, phosphine selenides, selenoureas and selenocyanates are preferable.

[0095]

In the tellurium sensitization, an unstable tellurium

compound is used. Examples of such unstable tellurium compounds capable of being used include those as described, for example, in JP-A Nos. 4-224595, 4-271341, 4-333043, 5-303157, 6-27573, 6-175258, 6-180478, 6-208186, 6-208184, 6-317867, 7-140579, 7-301879, and 7-301880.

[0096]

Specifically, phosphine tellurides (for example, butyl-diisopropyl phosphine telluride, tributyl phosphine telluride, tributoxy phosphine telluride, and ethoxy-diphenyl phosphine telluride), diacyl (di)tellurides (for example, bis(diphenylcarbamoyl) ditelluride, bis(N-phenyl-N-methyl carbamoyl)ditelluride, bis(N-phenyl-N-methylcarbamoyl) telluride, bis(N-phenyl-N-benzylcarbamoyl) telluride, and bis(ethoxycarbonyl) telluride), telluroureas (for example, N,N'-dimethylethylene tellurourea, and N,N'-diphenylethylene tellurourea), telluroamides, telluroesters, and the like may be used. Particularly, the diacyl (di)tellurides and the phosphine tellurides are preferable and, further, compounds as described in paragraph [0030] of JP-A No. 11-65021 and compounds represented by the formulas (II), (III), and (IV) of JP-A No. 5-313284 are more preferable.

[0097]

Particularly, in the chalcogen sensitization according

to the invention, the selenium sensitization and the tellurium sensitization are preferable, and the tellurium sensitization is particularly preferable.

[0098]

In the gold sensitization, gold sensitizers as described in P. Grafkides, *Chimie et Physique Photographique*, 5th ed., Paul Momtel, (1987), and *Research Disclosure*, Vol. 307, No. 307105 can be used. Specific examples of the gold sensitizers include chloroauric acid, potassium chloroaurate, potassium aurithiocyanate, gold sulfide and gold selenide, and, further, gold compounds as described, for example, in USP Nos. 2642361, 5049484, 5049485, 5169751, and 5252455, and Belgian Patent No. 691857. Further, salts of other noble metals than gold such as platinum, palladium, and iridium as described in P. Grafkides, *Chimie et Physique Photographique*, 5th ed., Paul Momtel, (1987), and *Research Disclosure*, Vol. 307, No. 307105 can also be used.

[0099]

Although the gold sensitization can be used alone, it is preferably used in combination with the chalcogen sensitization. Specific examples thereof include gold-sulfur sensitization, gold-selenium sensitization, gold-tellurium sensitization, gold-sulfur-selenium sensitization, gold-sulfur-tellurium sensitization,

gold-selenium-tellurium sensitization, and  
gold-sulfur-selenium-tellurium sensitization.

[0100]

According to the invention, the chemical sensitization can be performed at any time so long as it is performed in a period of from after the grain is formed to before application is performed and timing of performing the chemical sensitization can be, after desalination, for example, (1) before spectral sensitization, (2) simultaneously with the spectral sensitization, (3) after the spectral sensitization, or (4) immediately before application.

[0101]

A quantity of the chalcogen sensitizer to be used according to the invention is, though varying depending on the silver halide grain to be used, chemical ripening conditions and the like, in a range from  $10^{-8}$  mol to  $10^{-1}$  mol, and preferably approximately from  $10^{-7}$  mol to  $10^{-2}$  mol per mol of silver halide in each case.

In a same manner as in the chalcogen sensitizer, a quantity of the gold sensitizer to be used according to the invention is, though varying depending on various types of conditions, as approximate numbers, in a range from  $10^{-7}$  mol to  $10^{-2}$  mol, and preferably from  $10^{-6}$  mol to  $5 \times 10^{-3}$  mol per mol of silver

halide in each case. As for environmental conditions under which the emulsion is chemically sensitized, any condition can be selected; however, pAg is 8 or less, preferably 7.0 or less, more preferably 6.5 or less, and particularly preferably 6.0 or less; pAg is 1.5 or more, preferably 2.0 or more, and particularly preferably 2.5 or more; pH is in a range from 3 to 10, and preferably from 4 to 9; and temperature is in a range from 20°C to 95°C and preferably approximately from 25°C to 80°C.

[0102]

According to the invention, reduction sensitization can be used simultaneously with the chalcogen sensitization or the gold sensitization. It is particularly preferable that the reduction sensitization is used simultaneously with the chalcogen sensitization.

Specific examples of preferred compounds which can be used in a reduction sensitization method include ascorbic acid, thiourea dioxide, and dimethylamine borane, as well as stannous chloride, aminoiminomethane sulfinic acid, hydrazine derivatives, borane compounds, silane compounds, and polyamines. Further, addition of a reduction sensitizer may be performed at any step in a manufacturing process of the photosensitive emulsion, that is, in a preparation process of from crystal growth to immediately before application. Still further, the reduction sensitization is preferably performed

by ripening the emulsion while maintaining the pH thereof at 8 or more, or the pAg thereof at 4 or less. Furthermore, the reduction sensitization is preferably performed by introducing a single addition portion of a silver ion during grain formation.

A quantity of the reduction sensitizer to be added is, though varying depending on various types of conditions in a same manner as in the chalcogen sensitizer or gold sensitizer, as approximate numbers, preferably in a range from  $10^{-7}$  mol to  $10^{-1}$  mol, and more preferably from  $10^{-6}$  mol to  $5 \times 10^{-2}$  mol per mol of silver halide in each case.

[0103]

In the silver halide emulsion according to the invention, a thiosulfonic acid compound may be added by a method as described in EP-A No. 293,917.

It is preferable from the standpoint of designing a high sensitive photothermographic material that the photosensitive silver halide grain according to the invention is chemically sensitized by at least one of the gold sensitization method and the chalcogen sensitization method.

[0104]

9) Compound In Which A One-Electron-Oxidized Form Generated By Oxidizing One Electron Therein Can Release One Or More Electrons



It is preferable that the photothermographic material according to the invention comprises a compound in which a one-electron-oxidized form generated by oxidizing one electron therein can release one or more electrons. The compound can be used alone or in combination with the various chemical sensitizers described above to increase the sensitivity of silver halide.

[0105]

The compound in which a one-electron-oxidized form generated by oxidizing one electron therein can release one or more electrons is a compound selected from the following types 1 to 5:

[0106]

(type 1) a compound in which a one-electron-oxidized form generated by oxidizing one electron therein, following a subsequent bond-cleavage reaction, can further release 2 or more electrons;

(type 2) a compound in which a one-electron-oxidized form generated by oxidizing one electron therein, following a subsequent bond-cleavage reaction, can further release another electron and in which 2 adsorptive groups to silver halide are present in a same molecule;

(type 3) a compound in which a one-electron-oxidized form

generated by oxidizing one electron therein, after being subjected to a subsequent bond-forming step, can further release one or more electrons;

(type 4) a compound in which a one-electron-oxidized form generated by oxidizing one electron therein, after being subjected to a subsequent ring-cleavage reaction in a molecule, can further release one or more electrons; and

(type 5) a compound represented by X-Y in which X represents a reducing group, Y represents a dissociating group, and the reducing group represented by X in which a one-electron-oxidized form generated by oxidizing one electron therein, following a subsequent cleavage reaction of an X-Y bond, dissociates Y to generate an X radical from which another electron can further be released.

[0107]

Among compound types 1 and 3 to 5, preferable is "a compound having an adsorptive group to silver halide in a molecule", or "a compound having a partial structure of a spectral sensitizing dye in a molecule", and more preferable is "a compound having an adsorptive group to silver halide in a molecule". Among compound types 1 to 4, more preferable is "a compound having, as an adsorptive group, a nitrogen-containing heterocyclic group which is substituted by 2 or more mercapto groups".

[0108]

The compound types 1 to 5 will be described in detail below.

In regard to the compound type 1, the term "bond-cleavage reaction" is intended to mean a cleavage of a bond between elements in each of following combinations of elements: carbon-carbon, carbon-silicon, carbon-hydrogen, carbon-boron, carbon-tin, and carbon-germanium and, a cleavage of a bond in carbon-hydrogen may further follow. The compound type 1 is a compound which first becomes a one-electron-oxidized form by oxidizing one electron therein and, then, following the bond-cleavage reaction, can further release 2 or more (preferably 3) electrons.

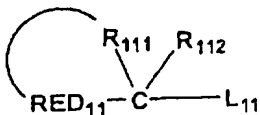
[0109]

A preferable compound of compound type 1 is represented by any one of the formulas (A) and (B), the formulas (1) to (3).

[0110]

[Formula 23]

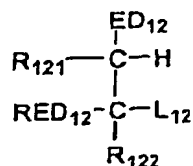
Formula (A)



[0111]

[Formula 24]

Formula (B)



[0112]

In the formula (A), RED<sub>11</sub> represents a reducing group in which one electron can be oxidized; L<sub>11</sub> represents a dissociating group; R<sub>112</sub> represents a hydrogen atom or a substituent; and R<sub>111</sub> represents a non-metallic atomic group which can, together with a carbon atom (C) and RED<sub>11</sub>, form a ring structure corresponding to a tetrahydro form, a hexahydro form, or an octahydro form of a 5- or 6-membered aromatic ring (inclusive of aromatic heterocycle).

[0113]

In the formula (B), RED<sub>12</sub> represents a reducing group in which one electron can be oxidized; L<sub>12</sub> represents a dissociating group; R<sub>121</sub> and R<sub>122</sub> each individually represent a hydrogen atom or a substituent; and ED<sub>12</sub> represents an electron-donating group. In the formula (B), R<sub>121</sub> and RED<sub>12</sub>, R<sub>121</sub> and R<sub>122</sub>, or ED<sub>12</sub> and RED<sub>12</sub> may, within each individual combination, be combined with each

other to form a ring structure.

[0114]

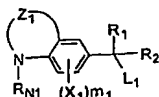
Compounds represented by the formula (A) or (B) are each a compound in which a reducing group represented by RED<sub>11</sub> or RED<sub>12</sub> can, after one electron therein is oxidized, spontaneously dissociate L<sub>11</sub> or L<sub>12</sub> by a bond-cleavage reaction and can, following such reaction, further release 2 or more, preferably 3 or more electrons.

[0115]

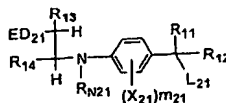
Formula (1), Formula (2), Formula (3)

[Formula 25]

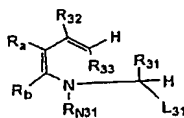
Formula (1)



Formula (2)



Formula (3)



[0116]

In the formula (1), Z<sub>1</sub> represents an atomic group which can form a 6-membered ring, together with a nitrogen atom and 2 carbon atoms of a benzene ring; R<sub>1</sub>, R<sub>2</sub>, and R<sub>N1</sub> each individually represent a hydrogen atom or a substituent; X<sub>1</sub> represents a substituent which can be substituted in a benzene ring; m<sub>1</sub>

represents an integer of 0 to 3; and  $L_1$  represents a dissociating group. In the formula (2),  $ED_{21}$  represents an electron-donating group;  $R_{11}$ ,  $R_{12}$ ,  $R_{N21}$ ,  $R_{13}$ , and  $R_{14}$  each individually represent a hydrogen atom or a substituent;  $X_{21}$  represents a substituent which can be substituted in a benzene ring;  $m_{21}$  represents an integer of 0 to 3; and  $L_{21}$  represents a dissociating group.  $R_{N21}$ ,  $R_{13}$ ,  $R_{14}$ ,  $X_{21}$ , and  $ED_{21}$  may be combined with one another to form a ring structure. In the formula (3),  $R_{32}$ ,  $R_{33}$ ,  $R_{31}$ ,  $R_{N31}$ ,  $R_a$ , and  $R_b$  each individually represent a hydrogen atom or a substituent; and  $L_{31}$  represents a dissociating group. When  $R_{N31}$  represents a group exclusive of an aryl group,  $R_a$  and  $R_b$  are combined with each other to form an aromatic ring.

[0117]

Compounds as described above are each a compound which, after one electron therein is oxidized, can spontaneously dissociate  $L_1$ ,  $L_{21}$ , or  $L_{31}$  by a bond-cleavage reaction and can, following such reaction, further release 2 or more, preferably 3 or more electrons.

[0118]

First of all, compounds represented by the formula (A) will be described in detail below.

In the formula (A), a reducing group, in which one electron can be oxidized, represented by  $RED_{11}$  is a group which can be

combined with  $R_{111}$ , as described below, to form a specified ring. Specifically mentioned is a divalent group which is prepared by removing a hydrogen atom at a site appropriate for forming a ring structure from each of monovalent groups as described below. For example, mentioned are an alkylamino group, an arylamino group (such as an anilino group or a naphthylamino group), a heterocycloamino group (such as a benzthiazolylamino group or a pyrrolylamino group), an alkylthio group, an arylthio group (such as a phenylthio group), a heterocyclothio group, an alkoxy group, an aryloxy group (such as a phenoxy group), a heterocycloxy group, an aryl group (such as a phenyl group, a naphthyl group, or an anthranyl group), and an aromatic or non-aromatic heterocyclic group (a 5- to 7-membered, monocyclic or condensed-ring-type heterocycle having at least one heteroatom of a nitrogen atom, a sulfur atom, an oxygen atom, and a selenium atom; specific examples of such heterocycles include a tetrahydroquinoline ring, a tetrahydroisoquinoline ring, a tetrahydroquinoxaline ring, a tetrahydroquinazoline ring, an indoline ring, an indole ring, an indazole ring, a carbazole ring, a phenoxazine ring, a phenothiazine ring, a benzothiazoline ring, a pyrrole ring, a indazole ring, a thiazoline ring, a piperidine ring, a pyrrolidine ring, a morpholine ring, a benzimidazole ring, a benzimidazoline ring, a benzoxazoline ring, and a methylenedioxyphenyl ring) (hereinafter, compounds represented by  $RED_{11}$  are recited in terms

of respective monovalent groups thereof for the purpose of convenience). The compounds represented by RED<sub>11</sub> may each have a substituent.

[0119]

The substituent according to the invention means, unless otherwise specified, a substituent selected from the following groups: a halogen atom, an alkyl group (inclusive of an aralkyl group, a cycloalkyl group or an active methine group), an alkenyl group, an alkynyl group, an aryl group, a heterocyclic group (a position to be substituted is not limited), a heterocyclic group having a quaternized nitrogen atom (for example, a pyridinio group, an imidazolio group, a quinolinio group, or an isoquinolinio group), an acyl group, an alkoxycarbonyl group, an aryloxy carbonyl group, a carbamoyl group, a carboxyl group or a salt thereof, a sulfonyl carbamoyl group, an acyl carbamoyl group, a sulfamoyl carbamoyl group, a carbazoyl group, an oxalyl group, an oxamoyl group, a cyano group, a carbonimidoyl group, a thiocarbamoyl group, a hydroxyl group, an alkoxy group (inclusive of a group having a recurring unit of an ethyleneoxy group or a propyleneoxy group), an aryloxy group, a heterocycloxy group, an acyloxy group, an (alkoxy or aryloxy) carbonyloxy group, a carbamoyloxy group, a sulfonyloxy group, an amino group, (an alkyl, aryl, or a heterocyclo) amino group, an acylamino group, a sulfonamide group, a ureido group, a thioureido group,



an imido group, an (alkoxy or aryloxy) carbonylamino group, a sulfamoylamino group, a semicarbazide group, a thiosemicarbazide group, a hydrazino group, an ammonio group, an oxamoylamino group, an (alkyl or aryl) sulfonylureido group, an acylureido group, an acylsulfamoylamino group, a nitro group, a mercapto group, (an alkyl, aryl, or a heterocyclo) thio group, an (alkyl or aryl) sulfonyl group, an (alkyl or aryl) sulfinyl group, a sulfo group or a salt thereof, a sulfamoyl group, an acylsulfamoyl group, a sulfonylsulfamoyl group or a salt thereof, and a group having a phosphoramidate or phosphoric acid ester structure. These substituents may each be further substituted by any one of these substituents.

[0120]

The compound represented by RED<sub>11</sub> is preferably an alkylamino group, an arylamino group, a heterocycloamino group, an aryl group, or an aromatic or non-aromatic heterocyclic group, and more preferably an arylamino group (particularly an anilino group), or an aryl group (particularly a phenyl group). When these groups each have a substituent, the substituent is preferably a halogen atom, an alkyl group, an alkoxy group, a carbamoyl group, a sulfamoyl group, an acylamino group, or a sulfonamide group.

When RED<sub>11</sub> represents an aryl group, the aryl group preferably has at least one "electron-donating group". The

term "electron-donating group" is intended to include a hydroxyl group, an alkoxy group, a mercapto group, a sulfonamide group, an acylamino group, an alkylamino group, an arylamino group, a heterocycloamino group, and an active methine group, a 5-membered, monocyclic or condensed-ring-type, electron-excessive aromatic heterocyclic group having at least one nitrogen atom in a cycle (for example, an indolyl group, a pyrrolyl group, an imidazolyl group, a benzimidazolyl group, a thiazolyl group, a benzthiazolyl group, or an indazolyl group), a nitrogen-containing heterocyclic group substituted by a nitrogen atom (a group capable of being called as a cycloamino group such as a pyrrolidinyl group, an indolinyl group, a piperidinyl group, a piperazinyl group, or a morpholino group). The active methine group on this occasion means a methine group substituted by two "electron-attracting groups"; examples of such electron-attracting groups include an acyl group, an alkyloxycarbonyl group, an aryloxycarbonyl group, a carbamoyl group, an alkylsulfonyl group, an arylsulfonyl group, a sulfamoyl group, a trifluoromethyl group, a cyano group, a nitro group, or a carbonimidoyl group. On this occasion, two electron-attracting groups may be combined with each other to form a ring structure.

[0121]

In the formula (A),  $L_{11}$  specifically represents a carboxyl

group or a salt thereof, a silyl group, a hydrogen atom, a triarylboroanion, a trialkylstannyl group, a trialkylgermyl group, or a  $-CR_{C1}R_{C2}R_{C3}$  group. Specific examples of such silyl groups include a trialkylsilyl group, an aryldialkylsilyl group, and a triarylsilyl group. The silyl groups may each have a given substituent.

[0122]

When  $L_{11}$  represents a salt of a carboxyl group, examples of counter ions which each form the salt include an alkaline metal ion, an alkaline earth metal ion, a heavy metal ion, an ammonium ion, and a phosphonium ion, in which an alkaline metal ion or an ammonium ion is preferable, and an alkaline metal ion (particularly,  $Li^+$ ,  $Na^+$ , or  $K^+$  ion) is most preferable.

[0123]

When  $L_{11}$  represents a  $-CR_{C1}R_{C2}R_{C3}$  group,  $R_{C1}$ ,  $R_{C2}$ , and  $R_{C3}$  each individually represent a hydrogen atom, an alkyl group, an aryl group, a heterocyclic group, an alkylthio group, an arylthio group, an alkylamino group, an arylamino group, a heterocycloamino group, an alkoxy group, an aryloxy group, or a hydroxyl group, and these groups may be combined with one another to form a ring structure and, also, may each individually have a given substituent. When any one of  $R_{C1}$ ,  $R_{C2}$ , and  $R_{C3}$  represents a hydrogen atom or an alkyl group, the remaining

ones represent neither hydrogen nor alkyl group.  $R_{C1}$ ,  $R_{C2}$ , and  $R_{C3}$  each individually preferably represents an alkyl group, an aryl group (particularly phenyl group), an alkylthio group, an arylthio group, an alkylamino group, an arylamino group, a heterocyclic group, an alkoxy group, or a hydroxyl group. Specific examples thereof include a phenyl group, a p-dimethylaminophenyl group, a p-methoxyphenyl group, a 2,4-dimethoxyphenyl group, a p-hydroxyphenyl group, a methylthio group, a phenylthio group, a phenoxy group, a methoxy group, an ethoxy group, a dimethylamino group, an N-methylanilino group, a diphenylamino group, a morpholino group, a thiomorpholino group, and a hydroxy group. Further, these groups may be combined with each other to form a ring structure; examples of such groups include a 1,3-dithiolan-2-yl group, a 1,3-dithian-2-yl group, an N-methyl-1,3-thiazolidin-2-yl group, and an N-benzyl-benzothiazolidin-2-yl group.

It is also a preferable case in which a  $-CR_{C1}R_{C2}R_{C3}$  group represents a same group as a residue generated by removing  $L_{11}$  from the formula (A) as a result of selecting  $R_{C1}$ ,  $R_{C2}$ , and  $R_{C3}$  from within respective ranges as described above.

[0124]

In the formula (A),  $L_{11}$  is preferably a carboxyl group or a salt thereof, or a hydrogen atom, and more preferably a

carboxylic group or a salt thereof.

[0125]

When  $L_{11}$  represents a hydrogen atom, the compound represented by the formula (A) preferably has a base site inherent in a molecule. After the compound represented by the formula (A) is oxidized by an action of this base site, a hydrogen atom represented by  $L_{11}$  is deprotonated and, subsequently, an electron is released from the resultant deprotonated hydrogen atom.

[0126]

On this occasion, the base specifically denotes a conjugate base of an acid having from approximately 1 pKa to approximately 10 pKa. Examples of such bases include nitrogen-containing heterocycles (such as pyridines, imidazoles, benzimidazoles, and thiazoles), anilines, trialkylamines, an amino group, carbon acids (such as an active methylene anion), a thioacetic acid anion, a carboxylate ( $-\text{COO}^-$ ), a sulfate ( $-\text{SO}_3^-$ ), and an aminoxide ( $>\text{N}^+(\text{O}^-)-$ ). Conjugate bases of acids having from approximately 1 pKa to approximately 8 pKa are preferable, in which a carboxylate, a sulfate, and an aminoxide are more preferable, and a carboxylate is particularly preferable. When these bases each have an anion, these bases may each have a counterion; examples of such counterions include

an alkaline metal ion, an alkaline earth metal ion, a heavy metal ion, an ammonium ion, and a phosphonium ion. These bases are each individually linked to the compound represented by the formula (A) at a given position. The position at which these base sites are each individually connected to is any of RED<sub>11</sub>, R<sub>111</sub>, and R<sub>112</sub> represented by the formula (A) and, further, respective substituents thereof.

[0127]

In the formula (A), R<sub>112</sub> represents a hydrogen atom or a substituent which can be substituted to a carbon atom. However, R<sub>112</sub> and L<sub>11</sub> do not simultaneously represent a same group.

R<sub>112</sub> preferably represents a hydrogen atom, an alkyl group, an aryl group (for example, a phenyl group), an alkoxy group (for example, a methoxy group, an ethoxy group or a benzyloxy group), a hydroxyl group, an alkylthio group (for example, a methylthio group or a butylthio group), an amino group, an alkylamino group, an arylamino group, or a heterocycloamino group, and more preferably represents a hydrogen atom, an alkyl group, an alkoxy group, a hydroxyl group, a phenyl group or an alkylamino group.

[0128]

In the formula (A), the ring structure formed by R<sub>111</sub> is a ring structure corresponding to a tetrahydro form, a hexahydro

form or an octahydro form of a 5- or 6-membered aromatic ring (inclusive of an aromatic heterocycle). The term "hydro form" as used in the above description is intended to mean a ring structure in which a carbon-carbon double bond (or carbon-nitrogen double bond) inherent in an aromatic ring (inclusive of an aromatic heterocycle) is partially hydrogenated, while the terms "tetrahydro form", "hexahydro form", and "octahydro form" are intended to mean structures in which 2, 3, and 4 carbon-carbon double bonds (or corresponding numbers of carbon-nitrogen double bonds) are hydrogenated, respectively. The aromatic ring is converted into a non-aromatic ring structure by being partially hydrogenated.

Examples of such ring structures include a pyrrolidine ring, a imidazolidine ring, a thiazolidine ring, a pyrazolidine ring, an oxazolidine ring, a piperidine ring, a tetrahydropyridine ring, a tetrahydropyrimidine ring, a piperazine ring, a tetraline ring, a tetrahydroquinoline ring, a tetrahydroisoquinoline ring, a tetrahydroquinazoline ring, a tetrahydroquinoxaline ring, a tetrahydrocarbazole ring, and octahydrophenanthridine ring. These ring structures may each individually have a given substituent.

[0129]

The ring structures formed by  $R_{111}$  are more preferably a pyrrolidine ring, a imidazolidine ring, a piperidine ring,

a tetrahydropyridine ring, a tetrahydropyrimidine ring, a piperazine ring, a tetrahydroquinoline ring, a tetrahydroisoquinoline ring, a tetrahydroquinazoline ring, a tetrahydroquinoxaline ring and a tetrahydrocarbazole ring, and particularly preferably a pyrrolidine ring, a piperidine ring, a piperazine ring, a tetrahydropyridine ring, a tetrahydroquinoline ring, a tetrahydroisoquinoline ring, a tetrahydroquinazoline ring and a tetrahydroquinoxaline ring, and most preferably a pyrrolidine ring, a piperidine ring, a tetrahydropyridine ring, a tetrahydroquinoline ring, and a tetrahydroisoquinoline ring.

[0130]

In the formula (B),  $RED_{12}$  and  $L_{12}$  denote groups having same meanings as those as described in  $RED_{11}$  and  $L_{11}$  in the formula (A). Respective preferable ranges thereof are also same as those as described in  $RED_{11}$  and  $L_{11}$ . However,  $RED_{12}$  is monovalent except for a case in which it forms a ring structure as described below and, specifically, denotes same monovalent groups as those as described in  $RED_{11}$ .  $R_{121}$  and  $R_{122}$  denote groups having same meanings as those as described in  $R_{112}$  in the formula (A). Respective preferable ranges thereof are also same as those as described in  $RED_{112}$ .  $ED_{12}$  represents an electron-donating group.  $R_{121}$  and  $RED_{12}$ ,  $R_{121}$  and  $R_{122}$ , and  $ED_{12}$  and  $RED_{12}$  may, in each combination, be combined with each other to form a ring



structure.

[0131]

In the formula (B), an electron-donating group represented by  $ED_{12}$  is same as the electron-donating group as described as the substituent at the time  $RED_{11}$  represents an aryl group.  $ED_{12}$  preferably represents a hydroxyl group, an alkoxy group, a mercapto group, a sulfonamide group, an alkylamino group, an arylamino group, an active methine group, a 5-membered, monocyclic or condensed-ring-type, electron-excessive aromatic heterocyclic group having a nitrogen atom in a ring, a non-aromatic nitrogen-containing heterocyclic group substituted by a nitrogen atom, or a phenyl group substituted by any one of these electron-donating groups, and more preferably represents a hydroxyl group, a mercapto group, a sulfonamide group, an alkylamino group, an arylamino group, an active methine group, a non-aromatic nitrogen-containing heterocyclic group substituted by a nitrogen atom, or a phenyl group substituted by any one of these electron-donating groups (for example, a p-hydroxyphenyl group, a p-dialkylaminophenyl group, or an o,p-dialkoxyphenyl group).

[0132]

In the formula (B),  $R_{121}$  and  $RED_{12}$ ,  $R_{122}$  and  $R_{121}$ , or  $ED_{12}$  and  $RED_{12}$  may, in each combination, be combined with each other

to form a ring structure. The term "ring structure" formed on this occasion denotes a non-aromatic carbocyclic or heterocyclic, 5- to 7-membered, monocyclic or condensed-ring-type, substituted or non-substituted ring structure. When  $R_{121}$  and  $RED_{12}$  forms a ring structure, specific examples of such ring structures include not only examples of those formed by  $R_{111}$  in the formula (A), but also a pyrroline ring, an imidazoline ring, a thiazoline ring, a pyrazoline ring, an oxazoline ring, an indane ring, a morpholine ring, an indoline ring, a tetrahydro-1,4-oxazine ring, a 2,3-dihydrobenzo-1,4-oxazine ring, a tetrahydro-1,4-thiazine ring, a 2,3-dihydrobenzo-1,4-thiazine ring, a 2,3-dihydrobenzofuran ring, and a 2,3-dihydrobenzothiophene ring. When  $ED_{12}$  and  $RED_{12}$  forms a ring structure therebetween,  $ED_{12}$  preferably represents an amino group, an alkylamino group, or arylamino group. Specific examples of such ring structures to be formed include a tetrahydropyrazine ring, a piperazine ring, a tetrahydroquinoxaline ring, and a tetrahydroisoquinoline ring. When  $R_{122}$  and  $R_{121}$  forms a ring structure with each other, specific examples of such ring structures include a cyclohexane ring and a cyclopentane ring.

[0133]

Next, the formulas (1) to (3) will be described.

In the formulas (1) to (3), meanings of  $R_1$ ,  $R_2$ ,  $R_{11}$ ,  $R_{12}$ ,

and  $R_{31}$  are each same as that of  $R_{112}$  in the formula (A) and respective preferable ranges thereof are each also same as that of  $R_{112}$ .  $L_1$ ,  $L_{21}$ , and  $L_{31}$  each represent same dissociating group as that illustrated in  $L_{11}$  in the formula (A) and the preferable ranges thereof are each also same as that of  $L_{11}$ . Substituents represented by  $X_1$ , and  $X_{21}$  are each same as that illustrated in  $RED_{11}$  in the formula (A) at the time it has a substituent and respective preferable ranges thereof are each also same as that of  $RED_{11}$ .  $m_1$ , and  $m_{21}$  are each preferably an interger of 0 to 2, and more preferably an integer of 0 or 1.

[0134]

When  $R_{N1}$ ,  $R_{N21}$ , and  $R_{N31}$  each represent a substituent, such substituents are preferably an alkyl group, an aryl group, and a heterocyclic group, and the substituents may each further have a given substituent.  $R_{N1}$ ,  $R_{N21}$ , and  $R_{N31}$  are each preferably a hydrogen atom, an alkyl group or an aryl group, and more preferably a hydrogen atom or an alkyl group.

[0135]

When  $R_{13}$ ,  $R_{14}$ ,  $R_{33}$ ,  $R_a$ , and  $R_b$  each represent a substituent, preferable examples of such substituents include an alkyl group, an aryl group, an acyl group, an alkoxycarbonyl group, a carbamoyl group, a cyano group, an alkoxy group, an acylamino group, a sulfonamide group, a ureido group, a thioureido group,

an alkylthio group, an arylthio group, an alkylsulfonyl group, an arylsulfonyl group, and a sulfamoyl group.

[0136]

In the formula (1), a 6-membered ring formed by  $Z_1$  is a non-aromatic heterocycle condensed with a benzene ring and, specifically, as ring structures together with a benzene ring to be condensed, mentioned are a tetrahydroquinoline ring, a tetrahydroquinoxaline ring, and tetrahydroquinazoline ring, in which a tetrahydroquinoline ring, and a tetrahydroquinoxaline ring are preferable. These rings may each have a substituent.

[0137]

In the formula (2),  $ED_{21}$  is a group having a same meaning as that of  $ED_{12}$  and a preferable range thereof is also same as that of  $ED_{12}$ .

[0138]

In the formula (2), any two of  $R_{N21}$ ,  $R_{13}$ ,  $R_{14}$ ,  $X_{21}$  and  $ED_{21}$  may be combined with each other to form a ring structure. When  $R_{N21}$  and  $X_{21}$ , as an example thereamong, are combined to form a ring structure, the ring structure is preferably a 5- to 7-membered non-aromatic carbocycle or heterocycle; specific examples of such ring structures include a tetrahydroquinoline

ring, a tetrahydroquinoxaline ring, an indoline ring, and a 2,3-dihydro-5,6-benzo-1,4-thiazine ring. Thereamong, preferable are a tetrahydroquinoline ring, a tetrahydroquinoxaline ring, and an indoline ring.

[0139]

In the formula (3), when  $R_{N31}$  represents a group except an aryl group,  $R_a$  and  $R_b$  are combined with each other to form an aromatic ring. The term "aromatic ring" as used in the above description is intended to include an aryl group (for example, a phenyl group, or a naphthyl group) or an aromatic heterocyclic group (for example, a pyridine ring group, a pyrrole ring group, a quinoline ring group, or an indole ring group), in which an aryl group is preferable. The aromatic ring group may have a given substituent.

In the formula (3), it is a preferable case in which  $R_a$  and  $R_b$  are combined with each other to form an aromatic ring (particularly a phenyl group).

[0140]

In the formula (3),  $R_{32}$  preferably represents a hydrogen atom, an alkyl group, an aryl group, a hydroxyl group, an alkoxy group, a mercapto group, or an amino group. When  $R_{32}$  represents a hydroxyl group, it is a preferable case in which  $R_{33}$  simultaneously represents an "electron-attracting group".

The term "electron-attracting group" as used in the above description is same as in the previous description; examples of preferable electron-attracting groups include an acyl group, an alkoxycarbonyl group, a carbamoyl group, and a cyano group.

[0141]

Next, compound type 2 will be described.

The term "bond-cleavage reaction" as used in the compound type 2 is intended to include a cleavage of a bond between elements in each combination of carbon-carbon, carbon-silicon, carbon-hydrogen, carbon-boron, carbon-tin, and carbon-germanium and, further, a cleavage of a carbon-hydrogen bond may follow any of these cleavages.

[0142]

The compound type 2 has 2 or more (preferably 2 to 6, and more preferably 2 to 4) adsorptive groups to silver halide in a molecule. The compound type 2 is preferably a compound which has, as an adsorptive group, a nitrogen-containing heterocyclic group substituted with 2 or more mercapto groups. A number of such adsorptive groups is preferably 2 to 6, and more preferably 2 to 4. The adsorptive group will be described in detail below.

[0143]

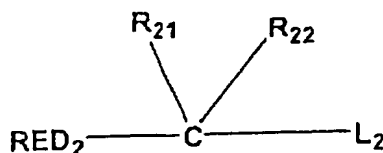
Preferable compound of the compound type 2 is represented by the following formula (C):

[0144]

Formula (C)

[Formula 26]

Formula (C)



[0145]

The compound represented by the formula (C) denotes a compound which, after a reducing group represented by RED<sub>2</sub> is one-electron-oxidized and the thus-oxidized reducing group spontaneously dissociates L<sub>2</sub> by the bond-cleavage reaction, can further release another electron following such dissociation.

[0146]

RED<sub>2</sub> in the formula (C) denotes a group having a same meaning as that of RED<sub>12</sub> and a preferable range of RED<sub>2</sub> is also same as that of RED<sub>12</sub>. L<sub>2</sub> denotes a group having a same meaning as that in the above description of L<sub>11</sub> in the formula (A) and a preferable range of L<sub>2</sub> is also same as that of L<sub>11</sub>. When L<sub>2</sub>

represents a silyl group, the compound, namely, the silyl group, refers to a compound which has, as reducing group, a nitrogen-containing heterocyclic group substituted by 2 or more mercapto groups in a molecule.  $R_{21}$  and  $R_{22}$  each individually represent a hydrogen atom or a substituent and denote a group having same meaning and preferable range as those of  $R_{112}$  in the formula (A), respectively.  $RED_2$  and  $R_{21}$  may be combined with each other to form a ring structure.

[0147]

The ring structure to be formed on the above occasion denote a 5- to 7-membered, monocyclic or condensed-ring-type, non-aromatic carbocycle or heterocycle which may have a substituent. However, the ring structure is by no means a ring structure corresponding to a tetrahydro form, a hexahydro form or an octahydro form of an aromatic ring or an aromatic heterocycle. The ring structure is preferably a ring structure corresponding to a dihydro form of an aromatic ring or an aromatic heterocycle. Examples of such ring structures include a 2-pyrroline ring, a 2-imidazoline ring, a 2-thiazoline ring, a 1,2-dihydropyridine ring, a 1,4-dihydropyridine ring, an indoline ring, a benzimidazoline ring, a benzothiazoline ring, a benzoxazoline ring, a 2,3-dihydrobenzothiophene ring, a 2,3-dihydrobenzofuran ring, a benzo- $\alpha$ -pyran ring, a 1,2-dihydroquinoline ring, a 1,2-dihydroquinazoline ring, and



a 1,2-dihydroquinoxaline ring, in which a 2-imidazoline ring, a 2-thiazoline ring, an indoline ring, a benzimidazoline ring, a benzothiazoline ring, a benzoxazoline ring, a 1,2-dihydropyridine ring, a 1,2-dihydroquinoline ring, a 1,2-dihydroquinazoline ring and a 1,2-dihydroquinoxaline ring are preferable; and an indoline ring, a benzimidazoline ring, a benzothiazoline ring, a 1,2-dihydroquinoline ring are more preferable and an indoline ring is particularly preferable.

[0148]

Next, compound type 3 will be described.

The term "bond-forming step" as used in the compound type 3 is intended to denote a step of forming a bond between atoms in, for example, combinations of carbon-carbon, carbon-nitrogen, carbon-sulfur, and carbon-oxygen.

[0149]

The compound type 3 is preferably a compound characterized in that a one-electron-oxidized form generated by oxidizing one electron therein is allowed to subsequently react with a reactive group site (a non-aromatic heterocyclic group site of a carbon-carbon double bond site, a carbon-carbon triple bond site, an aromatic group site, or a benzo-condensed-ring site) which is simultaneously present in a molecule to form a bond and, then, can release further one or more electrons.

[0150]

In more detail, the compound type 3 has a characteristic that a one-electron-oxidized form generated by oxidizing one electron therein (a cationic radical species, or a neutral radical species generated by dissociating one proton therefrom) is allowed to react with the above-described reactive group which is simultaneously present in a same molecule to form a bond and, then, newly generates a radical species having a ring structure and, thereafter, following a direct or indirect dissociation of the proton from the radical species, a second electron is released therefrom.

Further, there is a case in which the two-electron oxidized form of the compound type 3, after being subjected to a hydrolysis reaction in one case or performing a tautomerization reaction directly accompanied by a transfer of a proton in another case, releases further one or more electrons, ordinarily two or more electrons. There is also another case in which the compound type 3 has capability of directly releasing further one or more electrons, ordinarily two or more electrons, from the two-electron-oxidized form thereof without passing through the tautomerization reaction.

[0151]

The compound type 3 is preferably represented by the

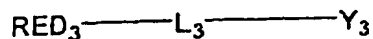
following formula (D):

[0152]

Formula (D)

[Formula 27]

Formula (D)



[0153]

In the formula (D), RED<sub>3</sub> represents a reducing group in which one electron can be oxidized; Y<sub>3</sub> represents a reactive group site which is reactive after one electron of RED<sub>3</sub> is oxidized and specifically represents an organic group having a carbon-carbon double bond site, a carbon-carbon triple bond site, an aromatic group site, or a benzo-condensed-ring, non-aromatic heterocyclic group site; and L<sub>3</sub> represents a linking group which links RED<sub>3</sub> and Y<sub>3</sub>.

[0154]

RED<sub>3</sub> in the formula (D) represents a group having a same meaning as that of RED<sub>12</sub> in the formula (B) and preferably represents an arylamino group, a heterocyclic amino group, an aryloxy group, an arylthio group, an aryl group, or an aromatic or non-aromatic heterocyclic group (particularly preferably

a nitrogen-containing heterocyclic group), and more preferably an arylamino group, a heterocyclic amino group, an aryl group, or an aromatic or non-aromatic heterocyclic group; examples of preferable heterocyclic groups include a tetrahydroquinoline ring group, a tetrahydroquinoxaline ring group, a tetrahydroquinazoline ring group, an indoline ring group, an indole ring group, a carbazole ring group, a phenoxazine ring group, phenothiazine ring group, a benzothiazoline ring group, a pyrrole ring group, an indazole ring group, a thiazole ring group, a benzimidazole ring group, a benzimidazoline ring group, a benzothiazoline ring group, and a 3,4-methylenedioxyphenyl-1-yl group.

Particularly preferable examples of RED<sub>3</sub> include an arylamino group (particularly an anilino group), an aryl group (particularly a phenyl group), and an aromatic or non-aromatic heterocyclic group.

[0155]

When RED<sub>3</sub> represents an aryl group, the aryl group preferably has at least one "electron-donating group". The "electron-donating group" in the above description has a same meaning as that as previously described.

[0156]

When RED<sub>3</sub> represents an aryl group, the aryl group may

have a substituent; examples of such substituents include an alkylamino group, a hydroxyl group, an alkoxy group, a mercapto group, a sulfonamide group, an active methine group, and a non-aromatic nitrogen-containing heterocyclic group substituted by a nitrogen atom, more preferable examples thereof include an alkylamino group, a hydroxyl group, an active methine group, and a non-aromatic nitrogen-containing heterocyclic group substituted by a nitrogen atom, and most preferable examples thereof include an alkylamino group and a non-aromatic nitrogen-containing heterocyclic group substituted by a nitrogen atom.

[0157]

When an organic group having a carbon-carbon double bond site resubstituted by  $Y_3$  (for example, a vinyl group) has a substituent, examples of preferable substituents include an alkyl group, a phenyl group, an acyl group, a cyano group, an alkoxycarbonyl group, a carbamoyl group and an electron-donating group; examples of such electron-donating groups include an alkoxy group, a hydroxyl group (also permissible as a form protected by a silyl group such as a trimethylsilyloxy group, a t-butyldimethylsilyloxy group, a triphenylsilyloxy group, a triethylsilyloxy group, or a phenyldimethylsilyloxy group), an amino group, an alkylamino group, an arylamino group, a sulfonamide group, an active methine group, a mercapto group,

an alkylthio group, and a phenyl group having any one of these electron-donating group as a substituent.

[0158]

When the organic group having the carbon-carbon double bond site has a hydroxyl group as a substituent,  $Y_3$  comes to have a partial structure, namely  $>C_1=C_2(-OH)-$ . This partial structure may be tautomerized to be another partial structure, namely  $>C_1H-C_2(=O)-$ . Further, at this time, a case in which a substituent that is substituted to a  $C_1$  carbon is an electron-attracting group is also preferable and, as being the case,  $Y_3$  comes to have an "active methylene group" or a partial structure of the "active methine group". The electron-attracting group which can give the active methylene group or the partial structure of the methine group is same as that in the previous description of the active methine group.

[0159]

When an organic group (for example, an ethynyl group) having a carbon-carbon triple bond site represented by  $Y_3$  has a substituent, preferable examples of such substituents include an alkyl group, a phenyl group, an alkoxycarbonyl group, a carbamoyl group and an electron-donating group.

[0160]

When Y<sub>3</sub> represents an organic group having an aromatic group site, an aromatic group is preferably an aryl group (particularly a phenyl group) having an electron-donating group as a substituent or an indole ring group; examples of preferable electron-donating groups include a hydroxyl group (permissible as a form protected by a silyl group), an alkoxy group, an amino group, an alkylamino group, an active methine group, a sulfonamide group, and a mercaptan group.

[0161]

When Y<sub>3</sub> represents an organic group having a benzo-condensed-ring-type non-aromatic heterocyclic group site, a benzo-condensed-ring-type non-aromatic heterocyclic group is preferably that having an aniline structure therein as a partial structure; examples of such benzo-condensed-ring-type non-aromatic heterocyclic groups include an indoline ring group, a 1,2,3,4-tetrahydroquinoline ring group, a 1,2,3,4-tetrahydroquinoxaline ring group, and a 4-quinolone ring group.

[0162]

The reactive group represented by Y<sub>3</sub> is more preferably an organic group having a carbon-carbon double bond site, an aromatic group site, or a benzo-condensed-ring-type non-aromatic heterocyclic group, and still more preferably a

phenyl group having a carbon-carbon double bond site, or an electron-donating group as a substituent, an indole group, or a benzo-condensed-ring-type, non-aromatic heterocyclic group inherently having an aniline structure as a partial structure. It is further still more preferable that the carbon-carbon double bond site has at least one electron-donating group as a substituent.

[0163]

A case in which the reactive group represented by  $Y_3$ , as a result of being selected from within a range so far described, has a same partial structure as that of the reducing group respected by  $RED_3$  is also a preferable example of the compound represented by the formula (D).

[0164]

$L_3$  represents a linking group which links  $RED_3$  and  $Y_3$  with each other, and specifically represents a single bond, an alkylene group, an arylene group, an heterocyclic group, an -O- group, an -S- group, an -NR<sub>N</sub>- group, a -C(=O)- group, an -SO<sub>2</sub>- group, an -SO- group, a -P(=O) group, or any combinations thereof, in which R<sub>N</sub> represents a hydrogen atom, an alkyl group, an aryl group, or a heterocyclic group. The linking group represented by  $L_3$  may have a given substituent. Further, the linking group represented by  $L_3$  can be linked by substituting



one given hydrogen of each of  $RED_3$  and  $Y_3$  at given positions of the groups represented by  $RED_3$  and  $Y_3$ , respectively.

As examples of preferable  $L_3$ , mentioned are divalent linking groups including a single bond, an alkylene group (particularly a methylene group, an ethylene group, a propylene group), an arylene group (particularly a phenylene group), a  $-C(=O)-$  group, an  $-O-$  group, an  $-NH-$  group, an  $-N(alkyl)-$  group, and any combinations thereof.

[0165]

In regard to a group represented by  $L_3$ , when a cationic radical species ( $X^{\cdot+}$ ) or a radical species ( $X^{\cdot}$ ) which is generated by dissociating a proton therefrom, and a reactive group represented by  $Y_3$  are allowed to react with each other to form a bond, it is preferable that a group of atoms related with such reaction and bond-formation forms a 3- to 7-membered ring structure together with  $L_3$ . For this end, it is preferable that the radical species ( $X^{\cdot+}$  or  $X^{\cdot}$ ), the reactive group represented by  $Y$ , and  $L_3$  are all linked with one another to form a group of 3 to 7 atoms.

[0166]

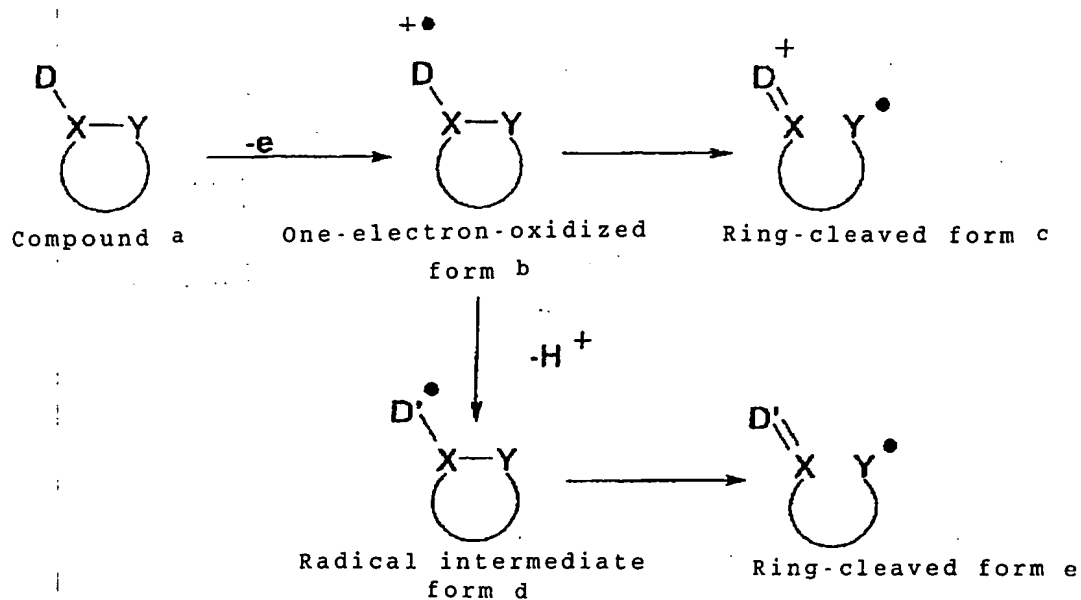
Next, compound type 4 will be described.

The compound type 4 denotes a compound having a ring structure substituted by a reducing group, and particularly

denotes a compound which, after the reducing group is one-electron-oxidized, following a cleavage reaction of a ring structure, can further release one or more electrons. The term "cleavage reaction of the ring structure" as used in the above description is represented by the following reaction scheme:

[0167]

[Formula 28]



[0168]

In the reaction scheme, the compound a denotes a compound type 4. In the compound a,  $D$  represents a reducing group; and  $X$ , and  $Y$  represent respective atoms which form a bond which is cleaved after one electron is oxidized. First, the compound

a is one-electron-oxidized to form a one-electron-oxidized form b and, then, a single bond of D-X in the thus-formed one-electron-oxidized form b is converted to a double bond and, at the same time, a bond of X-Y is cleaved to form a ring-cleaved form c. In another case in which the reaction passes through a path in which a radical intermediate d is generated by dissociating a proton from the thus-generated one-electron-oxidized form b and, then, a ring-cleaved form e is generated from the thus-generated radical intermediate d in a same manner as in the ring-cleaved form c. These compounds have characteristics in that one or more electrons are subsequently further released therefrom.

[0169]

The ring structure which the compound type 4 has denotes a 3- to 7-membered ring of a carbocycle or heterocycle and, particularly, denotes a monocyclic or condensed-ring-type, saturated or unsaturated non-aromatic ring. It is preferably a saturated ring structure, and more preferably a 3- or 4-membered ring structure. Examples of preferable ring structures include a cyclopropane ring, a cyclobutane ring, an oxirane ring, an oxetane ring, an aziridine ring, an azetidine ring, an episulfide ring, and a thietane ring, in which a cyclopropane ring, a cyclobutane ring, an oxirane ring, an oxetane ring, and an azetidine ring are more preferable and

a cyclopropane ring, a cyclobutane ring, and an azetidine ring are particularly preferable. These ring structures may each individually have a given substituent.

[0170]

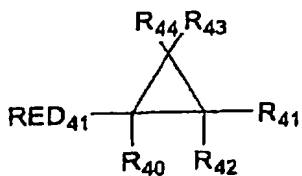
The compound type 4 is preferably represented by the following formula (E) or (F):

[0171]

Formula (E)

[Formula 29]

Formula (E)

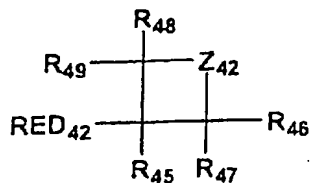


[0172]

Formula (F)

[Formula 30]

Formula (F)



[0173]

In the formulas (E) and (F), RED<sub>41</sub> and RED<sub>42</sub> each have a same meaning as that of RED<sub>12</sub> in the formula (B) and a preferable range of each of RED<sub>41</sub> and RED<sub>42</sub> is same as that of RED<sub>12</sub>. R<sub>40</sub> to R<sub>44</sub>, and R<sub>45</sub> to R<sub>49</sub>, each represent a hydrogen atom or a substituent. In the formula (F), Z<sub>42</sub> represents a -CR<sub>420</sub>R<sub>421</sub>- group, an -NR<sub>423</sub>- group, or an -O- group, in which R<sub>420</sub> and R<sub>421</sub> each represent a hydrogen atom or a substituent; and R<sub>423</sub> represents a hydrogen atom, an alkyl group, an aryl group or a heterocyclic group.

[0174]

In the formulas (E) and (F), R<sub>40</sub> and R<sub>45</sub> each represent preferably a hydrogen atom, an alkyl group, an aryl group or a heterocyclic group, and more preferably a hydrogen atom, an alkyl group or an aryl group. R<sub>41</sub> to R<sub>44</sub>, and R<sub>46</sub> to R<sub>49</sub>, each represent preferably a hydrogen atom, an alkyl group, an alkenyl group, an aryl group, a heterocyclic group, an arylthio group, an alkylthio group, an acylamino group or a sulfonamide group, and more preferably a hydrogen atom, an alkyl group, an aryl group or a heterocyclic group.

[0175]

Preferable is a case in which at least one of R<sub>41</sub> to R<sub>44</sub> is a donor-type group, or both of R<sub>43</sub> and R<sub>44</sub> are electron-attractive groups. More preferable is a case in which at least one of R<sub>41</sub> to R<sub>44</sub> is a donor-type group. Still more

preferable is a case in which not only at least one of  $R_{41}$  to  $R_{44}$  is a donor-type group, but also any one group which is not a donor type among  $R_{41}$  to  $R_{44}$  is a hydrogen atom or an alkyl group.

[0176]

The term "donor-type group" as used in the above description refers to an "electron-donating group, or an aryl group substituted by at least one "electron-donating group". As such donor-type groups, preferably used are an alkylamino group, an arylamino group, a heteroamino group, a 5-membered monocyclic or condensed-ring-type, electron-excessive aromatic heterocyclic group having at least one nitrogen atom in a cycle, a non-aromatic nitrogen-containing heterocyclic group substituted by a nitrogen atom, and a phenyl group substituted by at least one electron-donating group. More preferably used are an alkylamino group, an arylamino group, a 5-membered monocyclic or condensed-ring-type, electron-excessive aromatic heterocyclic group having a nitrogen atom in a cycle (for example, an indole ring, a pyrrole ring, or a carbazole ring), a phenyl group substituted by an electron-donating group (for example, a phenyl group substituted by 3 or more alkoxy groups, a phenyl group substituted by a hydroxyl group, an alkylamino group, or an arylamino group). Particularly preferably used are an arylamino group, a 5-membered monocyclic

or condensed-ring-type, electron-excessive, aromatic heterocyclic group having at least one of an arylamino group and a nitrogen atom in a ring (particularly a 3-indoline group), a phenyl group substituted by an electron-donating group (particularly a trialkoxyphenyl group, or a phenyl group substituted by an alkylamino group or an arylamino group).

[0177]

$Z_{42}$  represents preferably a  $-CR_{420}R_{421}$  group, or an  $-NR_{423}-$  group, and more preferably an  $-NR_{423}-$  group.  $R_{420}$ , and  $R_{421}$  each preferably represent a hydrogen group, an alkyl group, an aryl group, a heterocyclic group, an acylamino group and a sulfonamino group, and more preferably a hydrogen atom, an alkyl group, an aryl group and a heterocyclic group.  $R_{423}$  represents preferably a hydrogen atom, an alkyl group, an aryl group and an aromatic heterocyclic group, and more preferably a hydrogen atom, an alkyl group and an aryl group.

[0178]

When  $R_{40}$  to  $R_{49}$ ,  $R_{420}$ ,  $R_{421}$ , and  $R_{423}$  each represent a substituent, the substituent is preferably a substituent having 40 or less carbon atoms in total, and more preferably a substituent having 30 or less carbon atoms in total, and particularly preferably a substituent having 15 or less carbon atoms in total. Further, these substituents may be combined

with one another, or with another site (RED<sub>41</sub>, RED<sub>42</sub> or Z<sub>42</sub>) in a molecule to form a ring.

[0179]

The term "adsorptive group to silver halide" as used in the description of compound types 1 to 4 according to the invention refers to a group which is directly adsorbed to a silver halide or accelerates such adsorption to a silver halide and, specifically, refers to a mercapto group (or a salt thereof), a thione group ( $-C(=S)-$ ), a heterocyclic group having at least one atom selected from the group consisting of: a nitrogen atom, a sulfur atom, a selenium atom and a tellurium atom, a sulfide group, a cationic group, or an ethynyl group. However, a sulfide group is not contained as an adsorptive group in the compound type 2 according to the invention.

[0180]

The mercapto group (or a salt thereof) as the adsorptive group not only means the mercapto group itself, but also preferably refers to any one of a heterocyclic group, an aryl group and an alkyl group which have been substituted by at least one mercapto group (or a salt thereof). The above-described heterocyclic group refers to a 5- to 7-membered, monocyclic or condensed-ring-type aromatic or non-aromatic heterocyclic group. Examples of such heterocyclic groups include an



imidazole ring group, a thiazole ring group, an oxazole ring group, a benzimidazole ring group, a benzothiazole ring group, a benzoxazole ring group, a triazole ring group, a thiadiazole ring group, an oxadiazole ring group, a tetrazole ring group, a purine ring group, a pyridine ring group, a quinoline ring group, an isoquinoline ring group, a pyrimidine ring group, and a triazine ring group. Further, the heterocyclic group may be a heterocyclic group having a quaternized nitrogen atom; on this occasion, a substituted mercapto group may be dissociated to be a mesoion. Examples of such heterocyclic groups include an imidazolium ring group, a pyrazolium ring group, a thiazolium ring group, a tirazolium ring group, a tetrazolium ring group, a thiadiazolium ring group, a pyridinium ring group, a pyrimidinium ring group, and a triazinium ring group. Thereamong, preferable is a triazolium ring group (for example, a 1,2,4-triazolium-3-thiolate ring group). As the aryl group, mentioned is a phenyl group or a naphthyl group. As the alkyl group, mentioned is a straight, branched, or cyclic alkyl group having from 1 to 30 carbon atoms. When the mercapto group forms a salt, examples of counter ions include a cation ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Zn}^{2+}$  or the like) of an alkaline metal, an alkaline earth metal, a heavy metal or the like, an ammonium ion, a heterocyclic group having a quaternized nitrogen atom, and a phosphonium ion.

[0181]

The mercapto group as an adsorptive group may further be tautomerized to be a thione group. Specifically mentioned are a thioamide group (a  $\text{-C(=S)-NH-}$  group on this occasion), and a group which has a partial structure of the thioamido group, namely, a chained or cyclic thiamide group, a thioamido group, a thiourethane group, or a dithiocarbamic ester group. Examples of such cyclic groups include a thiazolidine-2-thione group, an oxazolidine-2-thione group, a 2-thiohydantoin group, a rhodanine group, an isorhodanine group, a thiobarbituric acid group, and a 2-thioxo-oxazolidin-4-one group.

[0182]

The thione groups as the adsorptive group include not only a thione group generated by tautomerizing the above-described mercapto group, but also a chained or cyclic thioamide group, thioureido group, thiourethane group or dithiocarbamic acid ester group which can not be tautomerized to the mercapto group (having no hydrogen atom at an  $\alpha$ -position of the thione group).

[0183]

The heterocyclic group having at least one atom selected from the group consisting of: a nitrogen atom, a sulfur atom, a selenium atom and a tellurium atom as an adsorptive group

denotes a nitrogen-containing heterocyclic group having an -NH- group which can form an imino silver ( $>N\text{Ag}$ ) as a partial structure of the heterocycle, or a heterocyclic group, having an -S- group, an -Se- group, a -Te- group, or an =N- group as a partial structure of a heterocycle, which can be bonded to a silver ion by a coordinate bond; examples of the former include a benzotriazole group, a triazole group, an indazole group, a pyrazole group, a tetrazole group, a benzimidazole group, an imidazole group, and a purine group; examples of the latter include a thiophene group, a thiazole group, an oxazole group, a benzothiazole group, a benzoxazole group, a thiadiazole group, an oxadiazole group, a triazine group, a selenazole group, a benzoselenazole group, a tellurazole group, and a benzotellurazole group. The former is preferable.

[0184]

The sulfide group as an adsorptive group denotes all of groups which each have an -S- group as a partial structure and preferably groups having a partial structure of alkyl (or alkylene)-S-alkyl (or alkylene), aryl (or arylene)-S-alkyl (or alkylene), or aryl (or arylene)-S-aryl (or arylene). Further, the sulfide group may form a ring structure, or be in a form of an -S-S- group. When the cyclic structure is formed, specifically mentioned is a group containing, for example, a thiolane ring, a 1,3-dithiolane ring or a 1,2-dithiolane ring,

a thiane ring, a dithiane ring, or a tetrahydro-1,4-thiazine ring (thiomorpholine ring). The sulfide group is particularly preferably a group having a partial structure of alkyl-(or alkylene)-S-alkyl (or alkylene).

[0185]

The cationic group as an adsorptive group means a group having a quaternized nitrogen atom and, specifically, refers to a group containing an ammonio group or a nitrogen-containing heterocyclic group having a quaternized nitrogen atom. However, the cationic group does not become a part of an atomic group forming a dye structure (for example, a cyanine chromophore). The ammonio group refers to a trialkylammonio group, a dialkylarylammonio group, an alkyl diarylammonio group or the like; examples of such ammonio groups include a benzyldimethylammonio group, a trihexylammonio group, and a phenyldiethylammonio group. As for the nitrogen-containing heterocyclic group having a quaternized nitrogen atom, mentioned are, for example, a pyridinio group, a quinolinio group, an isoquinolinio group, and an imidazolio group, in which a pyridinio group and an imidazolio group are preferable and a pyridinio group is particularly preferable. Any one of these nitrogen-containing heterocyclic groups each having a quaternized nitrogen atom may have a given substituent. However, when it refers to a pyridinio group or an imidazolio group,

the substituent is preferably an alkyl group, an aryl group, an acylamino group, a chlorine atom, an alkoxycarbonyl group, or a carbamoyl group. When it refers to a pyridinio group, the substituent is particularly preferably a phenyl group.

[0186]

The ethynyl group as an adsorptive group means a  $-C\equiv CH$  group in which a hydrogen atom may be substituted.

The above-described adsorptive groups may each have a given substituent.

[0187]

Specific examples of the adsorptive groups further include those as described in JP-A No. 11-95355, pp. 4 to 7.

[0188]

The adsorptive group according to the invention is preferably a mercapto-substituted nitrogen-containing heterocyclic group (for example, a 2-mercaptothiadiazole group, a 3-mercapto-1,2,4-triazole group, a 5-mercaptotetrazole group, a 2-mercapto-1,3,4-oxadiazole group, a 2-mercaptobenzoxazole group, a 2-mercaptobenzthiazole group, 1,5-dimethyl-1,2,4-triazolium-3-thiolate group), or a nitrogen-containing heterocyclic group having an  $-NH-$  group which can form an imino silver ( $>NAg$ ) as a partial structure

of a heterocycle (for example, a benzotriazole group, a benzimidazole group, or an indazole group), particularly preferably a 5-mercaptotetrazole group, a 3-mercapto-1,2,4-triazole group, or a benzotriazole group, and most preferably a 3-mercapto-1,2,4-triazole group, or a 5-mercaptotetrazole group.

[0189]

Among these compounds, a compound having two or more mercapto groups in a molecule as a partial structure is also preferable. The mercapto group (-SH) in the above-description may be tautomerized, if possible, to be a thione group. As for examples of such compounds, permissible is a compound which has two or more adsorptive groups (for example, ring-forming thioamide group, an alkylmercapto group, an arylmercapto group, and a heterocyclic mercapto group) having the above-described mercapto group or a thione group as a partial structure in a molecule, or a compound which has one or more adsorptive groups (for example, a dimercapto-substituted nitrogen-containing heterocyclic group) having two or more mercapto groups or thione groups as a partial structure in a molecule.

[0190]

Examples of the adsorptive groups (for example, dimercapto-substituted nitrogen-containing heterocyclic

group) each having two or more mercapto groups as a partial structure include a 2,4-dimercaptopyrimidine group, a 2,4-dimercaptotriazine group, a 3,5-dimercapto-1,2,4-triazole group, a 2,5-dimercapto-1,3-thiazole group, a 2,5-dimercapto-1,3-oxazole group, a 2,7-dimercapto-5-methyl-s-triazolo(1,5-A)-pyrimidine, 2,6,8-trimercaptopurine, a 6,8-dimercaptopurine, a 3,5,7-trimercapto-s-triazolotriazine, 4,6-dimercaptopyrazolopyrimidine, 2,5-dimercaptoimidazole in which a 2,4-dimercaptopyrimidine group, a 2,4-dimercaptotriazine group, and a 3,5-dimercapto-1,2,4-triazole group are particularly preferable.

[0191]

The adsorptive group may be substituted at any site of the formulas (A) to (F), and (1) to (3). However, the adsorptive group is preferably substituted at RED<sub>11</sub>, RED<sub>12</sub>, RED<sub>2</sub>, and RED<sub>3</sub> in the formulas (A) to (D), RED<sub>41</sub>, R<sub>41</sub>, RED<sub>42</sub>, and R<sub>46</sub> to R<sub>48</sub> in the formulas (E) and (F), and any given site except R<sub>1</sub>, R<sub>2</sub>, R<sub>11</sub>, R<sub>12</sub>, R<sub>31</sub>, L<sub>1</sub>, L<sub>21</sub>, and L<sub>31</sub> in the formulas (1) to (3), and more preferably at RED<sub>11</sub> to RED<sub>42</sub> in all of the formulas (A) to (F).

[0192]

The partial structure of the spectral sensitizing dye is a group having a chromophore of the spectral sensitizing dye and, also, is a residue generated by removing a given hydrogen or substituent from a spectral sensitizing dye compound. The partial structure of the spectral sensitizing dye may be substituted at any site in the formulas (A) to (F), and (1) to (3). However, the partial structure is preferably substituted at RED<sub>11</sub>, RED<sub>12</sub>, RED<sub>2</sub>, and RED<sub>3</sub> in the formulas (A) to (D), RED<sub>41</sub>, R<sub>41</sub>, RED<sub>42</sub>, and R<sub>46</sub> to R<sub>48</sub> in the formulas (E) and (F), and any given site except R<sub>1</sub>, R<sub>2</sub>, R<sub>11</sub>, R<sub>12</sub>, R<sub>31</sub>, L<sub>1</sub>, L<sub>21</sub>, and L<sub>31</sub> in the formulas (1) to (3), and more preferably at RED<sub>11</sub> to RED<sub>42</sub> in all of the formulas (A) to (F). Preferable spectral sensitizing dye is a spectral sensitizing dye to be typically used in a color sensitizing technique; examples of such spectral sensitizing dyes include cyanine dyes, complex cyanine dyes, merocyanine dyes, complex merocyanine dyes, homopolar cyanine dyes, styryl dyes, and hemicyanine dyes. Representative spectral sensitizing dyes are described in Research Disclosure, Item 36544, September, 1994. These dyes can be synthesized by those skilled in the art in accordance with procedures described in the Research Disclosure, or F. M. Hamer, The Cyanine dyes and Related Compounds (Interscience Publishers, New York, 1964). Further, dyes described in JP-A No. 11-95355, pp. 7 to 14, (USP No. 6,054,260) are all applicable to the spectral sensitizing dyes according to the invention.



[0193]

The compound types 1 to 4 according to the invention each have total carbon atoms in the range of preferably from 10 to 60, more preferably from 15 to 50, still more preferably from 18 to 40, and particularly preferably from 18 to 30.

[0194]

Each of the compound types 1 to 4 according to the invention is one-electron-oxidized by being triggered at exposing the silver halide photographic photosensitive material using any one of these compounds and, then, after a subsequent reaction, release one more electron, or two or more electrons depending on the types to be oxidized. An oxidation potential of a first electron is preferably approximately 1.4 V or less, and more preferably 1.0 V or less. The oxidation potential is preferably more than 0 V, more preferably more than 0.3 V. Therefore, the oxidation potential is preferably in a range from approximately 0 V to approximately 1.4 V, and more preferably from approximately 0.3 V to approximately 1.0 V.

[0195]

The oxidation potential can be measured by a cyclic voltammetry technique. Specifically, a sample is dissolved in a solution having a mixing ratio of 80%:20% (by volume) of

acetonitrile to water (containing 0.1 M lithium perchlorate). After a nitrogen gas is allowed to pass through the solution for 10 minutes, the resultant solution is subjected to measurements at 25°C with a potential scanning speed of 0.1 V/second by using a glassy carbon disc as a working electrode, a platinum wire as a counter electrode, and a calomel electrode (SCE) as a reference electrode. The oxidation potential vs. SCE is taken as a peak potential of a cyclic voltammetric wave.

[0196]

Each of the compound types 1 to 4 according to the invention is one-electron-oxidized and, then, after a subsequent reaction, release one more electron. An oxidation potential at this stage is preferably in a range from -0.5 V to -2 V, more preferably from -0.7 V to -2 V, and still more preferably from -0.9 V to -1.6 V.

[0197]

Each of the compound types 1 to 4 according to the invention is one-electron-oxidized and, then, after a subsequent reaction, release two or more electrons to be oxidized. An oxidation potential at this subsequent stage is not particularly limited. This is due to the fact that, since the oxidation potential of the second electron and those of a third electron and thereafter are not conspicuously distinguished, there are many

cases in which it is difficult to accurately measure these potentials in a separate manner.

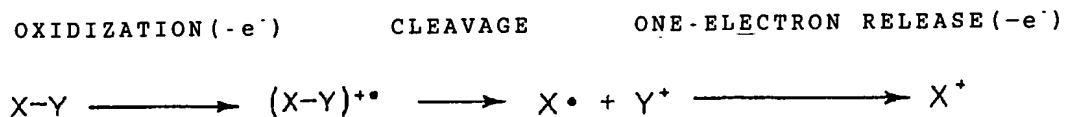
[0198]

Next, compound type 5 will be described.

The compound type 5 is represented by X-Y, in which X represents a reducing group; and Y represents a dissociating group each. The reducing group represented by X is a compound capable of being one-electron-oxidized to generate a one-electron-oxidized form and, then, following a subsequent cleavage reaction of an X-Y bond, the thus-formed one-electron-oxidized form dissociates Y therefrom to generate an X radical and, thereafter, the thus-generated X radical can release one more electron therefrom. Reactions at the time such compound type 5 as described above is oxidized can be represented by the following reaction formula:

[0199]

[Formula 31]



[0200]

An oxidation potential of the compound type 5 is preferably

in a range from 0 V to 1.4 V, and more preferably from 0.3 V to 1.0 V. An oxidation potential of a radical X· generated by the above reaction formula is preferably in a range from -0.7 V to -2.0 V, and more preferably from -0.9 V to -1.6 V.

[0201]

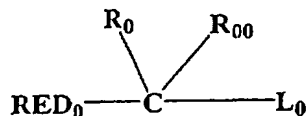
The compound type 5 is preferably represented by the following formula (G):

[0202]

Formula (G)

[Formula 32]

Formula (G)



[0203]

In the formula (G), RED<sub>0</sub> represents a reducing group; L<sub>0</sub> represents a dissociating group; R<sub>0</sub> and R<sub>00</sub> each represent a hydrogen atom or a substituent. RED<sub>0</sub> and R<sub>0</sub>, and R<sub>0</sub> and R<sub>00</sub> may, within each combination, be combined with each other to form a ring structure. RED<sub>0</sub> has a same meaning as that of RED<sub>2</sub> in the formula (C) and a preferable range thereof is also same as that of RED<sub>2</sub>. R<sub>0</sub> and R<sub>00</sub> have same meanings as those of R<sub>21</sub> and R<sub>22</sub> in the formula (C), respectively and preferable ranges

thereof are also same as those of  $R_{21}$  and  $R_{22}$  in the formula (C). However,  $R_0$  and  $R_{00}$  do not represent a group having a same meaning as that of  $L_0$  except a hydrogen atom.  $RED_0$  and  $R_0$  may be combined with each other to form a ring structure; examples of such ring structures include those in a case in which  $RED_2$  and  $R_{21}$  in the formula (C) are combined with each other to form a ring structure and preferable ranges thereof are also same as those of  $RED_2$  and  $R_{21}$  in the formula (C). Examples of ring structures formed by combining  $R_0$  and  $R_{00}$  with each other include a cyclopentane ring and a tetrahydrofuran ring.  $L_0$  in the formula (G) has a same meaning as that of  $L_2$  in the formula (C) and same is said with a preferable range thereof.

[0204]

The compounds represented by the formula (G) each preferably have an adsorptive group to silver halide or a partial structure of a spectral sensitizing dye in a molecule. When  $L_0$  represents a group except a silyl group, two or more adsorptive groups do not simultaneously exist in a molecule. However, two or more sulfide groups, without depending on  $L_0$ , may simultaneously be present in a molecule.

[0205]

Examples of such adsorptive groups to silver halide which the compounds represented by the formula (G) may have are same

as those of the reducing groups which the compound types 1 to 4 may have and, further, such examples include all of groups as described as the "adsorptive group to silver halide" in JP-A No. 11-95355, pp. 4 to 7, and same is said with the preferable range thereof.

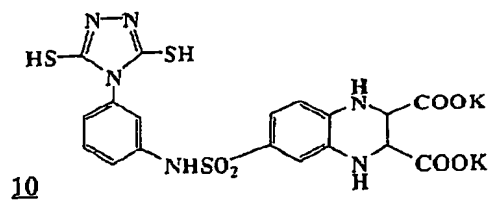
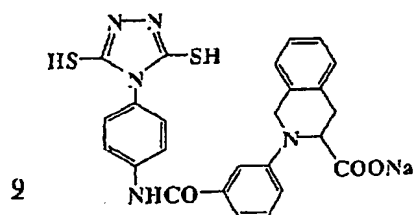
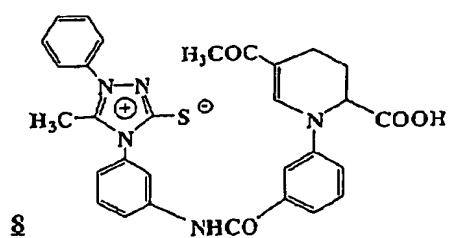
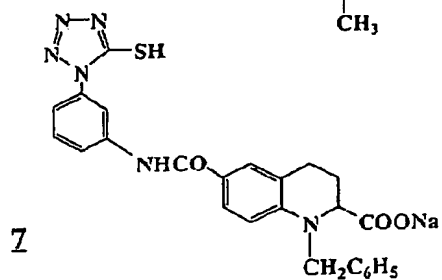
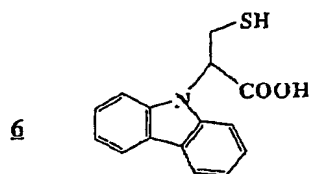
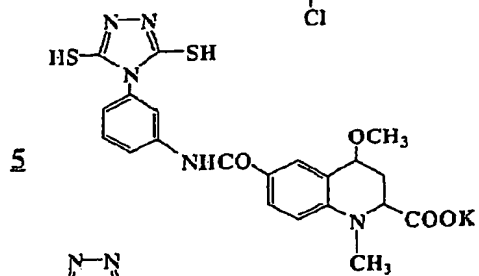
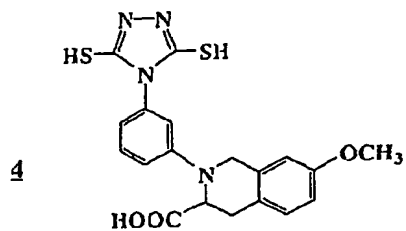
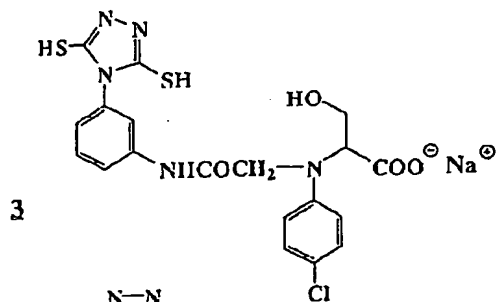
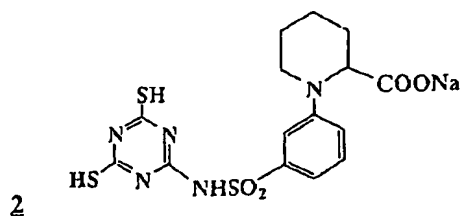
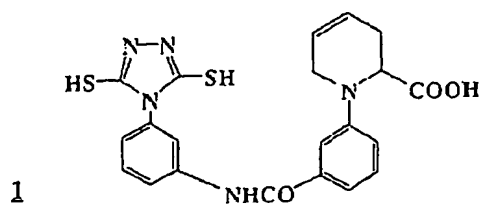
The partial structures of the spectral sensitizing dyes which the compounds represented by the formula (G) may have are same as those of the spectral sensitizing dyes which the compound types 1 to 4 may have and, at the same time, examples of such partial structures include all of the groups described as the "light-absorptive groups" in JP-A No. 11-95355, pp. 7 to 14, and same is said with the preferable range thereof.

[0206]

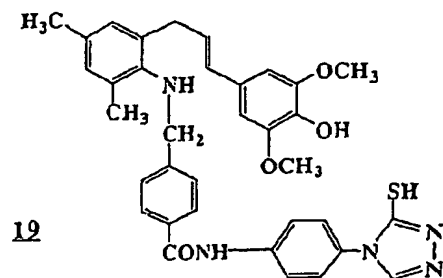
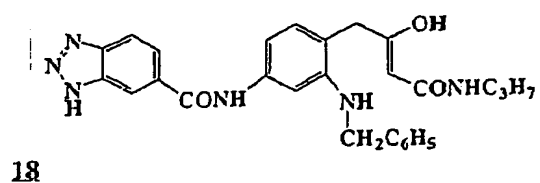
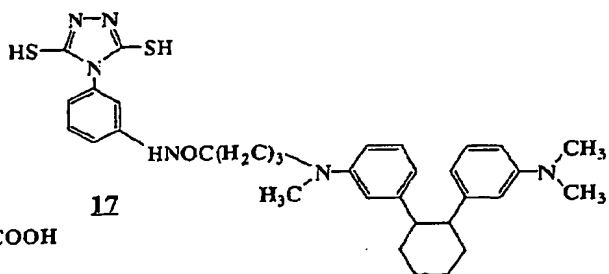
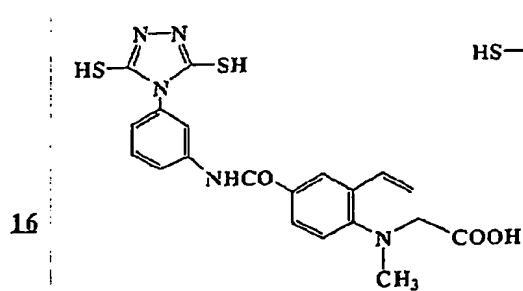
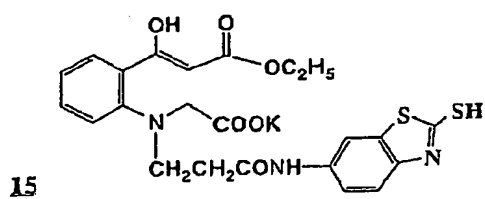
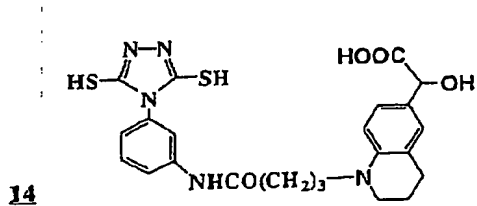
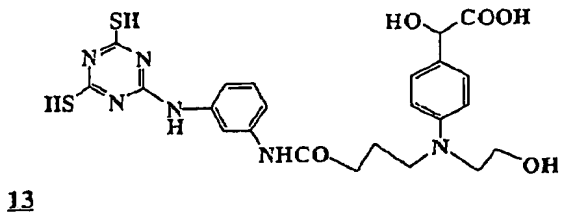
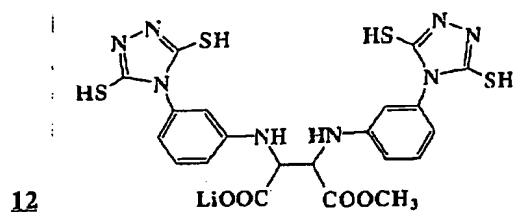
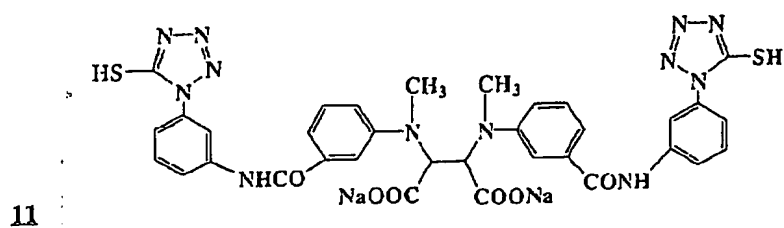
Specific examples of the compound types 1 to 5 according to the invention are described below; however, the invention is by no means limited thereto.

[0207]

[Formula 33]



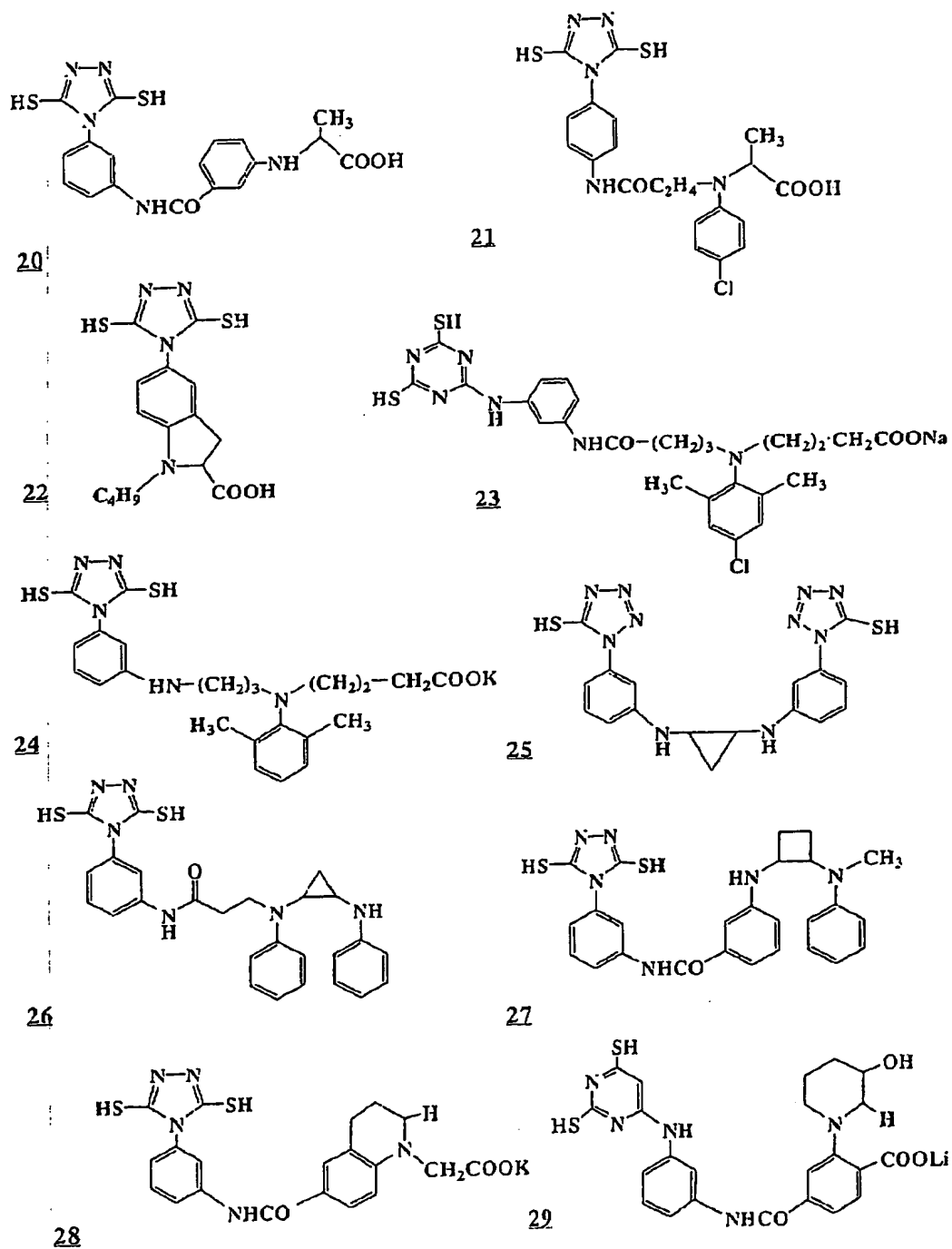
[Formula 34]





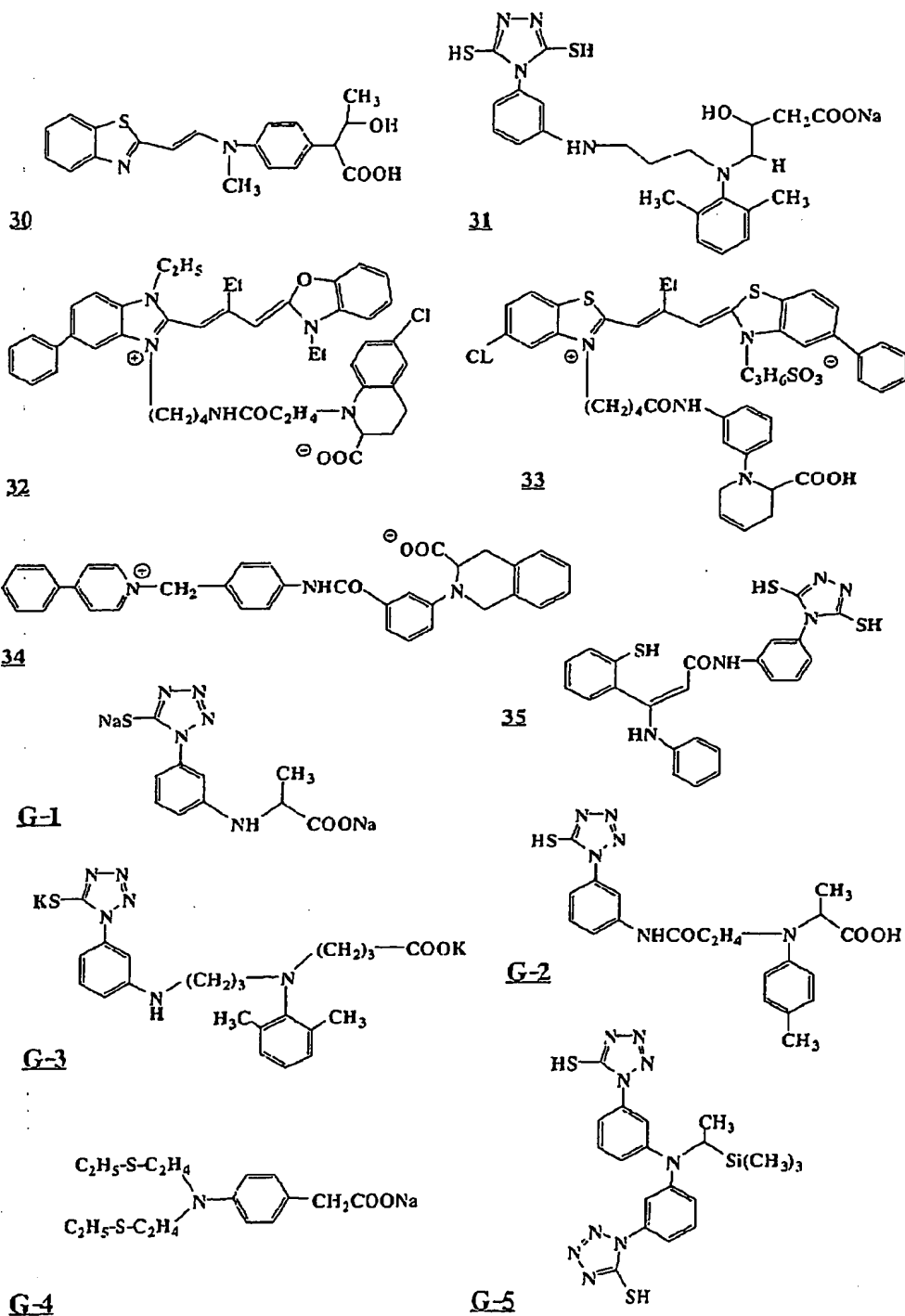
[0209]

[Formula 35]



[0210]

[Formula 36]



[0211]

The compound types 1 to 4 according to the invention are same as those as described in detail in Japanese Patent Application Nos. 2002-192373, 2002-188537, 2002-188536, 2001-272137, and 2002-192374. Specific examples of compounds as described in these patent applications are also applicable to examples of the compound types 1 to 4 according to the invention. Further, examples of syntheses of the compound types 1 to 4 according to the invention are same as those as described in these patent applications.

[0212]

As for specific examples of the compound type 5 according to the invention, examples of compounds denoted as "sensitizers capable of donating two electrons by one photon" or "deprotonating electron donating sensitizers" in, for example, JP-A No. 9-211769, pp. 28 to 32, Figs. E and F (compounds PMT-1 to S-37), JP-A No. 9-211774, JP-A No. 11-95355 (compounds INV1 to 36), JP-W No. 2001-500996 (compounds 1 to 74, 80 to 87, and 92 to 122), USP Nos. 5,747,235, 5,747,236, EP-A No. 786692A1 (compounds INV1 to 35), EP-A No. 893732 A1 and USP Nos. 6,054,260, and 5,994,051 are further mentioned as they are.

[0213]

The compound types 1 to 5 according to the invention may

be used at any step of the preparation process of the photosensitive silver halide or the production process of photothermographic material, for example, at a silver halide grain-forming step, at a desalting step, at the time of chemical sensitization, or before coating. The compounds can be added in 2 or more steps in a multiple addition manner. Addition time of the compounds is preferably from after completion of photosensitive silver halide grain formation to before the desalting step, at the time of chemical sensitization (from immediately before the start of chemical sensitization to immediately after the completion thereof), or before the coating, and more preferably from the time of chemical sensitization to before being mixed with a non-photosensitive organic silver salt.

[0214]

It is preferable that the compound types 1 to 5 according to the invention are each first dissolved in water, a water-soluble solvent, for example, methanol or ethanol, or mixtures thereof and, then, added. When the compound types 1 to 5 are dissolved in water, the compounds having a high solubility at a high or low pH may be dissolved while adjusting the pH thereof to be high or low and, then, added.

[0215]

The compound types 1 to 5 according to the invention are preferably used in an image-forming layer containing a photosensitive silver halide and a non-photosensitive organic silver salt; however, they may first be added not only to the image-forming layer containing the photosensitive silver halide and the non-photosensitive organic silver salt, but also to a protective layer and an intermediate layer and, then, be diffused at the time of coating. Addition timing of these compounds is not particularly limited; whether it is before or after the chemical sensitization is not questioned. The compounds are contained in a silver halide emulsion layer, based on 1 mol of silver halide, in a range from  $1 \times 10^{-9}$  mol to  $5 \times 10^{-1}$  mol, and preferably  $1 \times 10^{-8}$  to  $5 \times 10^{-2}$  mol.

[0216]

10) Compound Having Adsorptive group and Reducing Group

According to the invention, an adsorptive redox compound having an adsorptive group to silver and a reducing group in a molecule is preferably contained. Such compounds are preferably those represented by the following formula (I):

[0217]

Formula (I)       $A - (W)_n - B$

wherein A represents a group adsorptive to silver halide (hereinafter, referred to also as "adsorptive group");

W represents a divalent linking group;

n represents 0 or 1; and

B represents a reducing group.

[0218]

Next, the formula (I) will be described in detail.

In the formula (I), the adsorptive group represented by A is a group which is directly adsorptive to a silver halide, or a group which promotes such adsorption to the silver halide; and specific examples of such groups include a mercapto group (and a salt thereof), a thione group ( $-C(=S)-$ ), a heterocyclic group having at least one atom selected from the group consisting of: a nitrogen atom, a sulfur atom, a selenium atom and a tellurium atom, a sulfide group, a disulfide group, a cationic group, and an ethynyl group.

[0219]

The mercapto group (or a salt thereof) as the adsorptive group not only means a mercapto group itself but also preferably denotes any one of an heterocyclic group, an aryl group and an alkyl group which are each substituted by at least one mercapto group (or a salt thereof). The term "heterocyclic group" as used herein is intended to denote at least a 5- to 7-membered, monocyclic or condensed-ring-type, aromatic or non-aromatic heterocyclic group; examples of such heterocyclic groups

include an imidazole ring group, a thiazole ring group, an oxazole ring group, a benzimidazole ring group, a benzothiazole ring group, a benzoxazole ring group, a triazole ring group, a thiadiazole ring group, an oxadiazole ring group, a tetrazole ring group, a purine ring group, a pyridine ring group, a quinoline ring group, an isoquinoline ring group, a pyrimidine ring group, and a triazine ring group. Further, the heterocyclic group may be a heterocyclic group having a quaternized nitrogen atom; on this occasion, a substituted mercapto group may be dissociated to be a mesoion. Examples of such heterocyclic groups include an imidazolium ring group, a pyrazolium ring group, a thiazolium ring group, a tirazolium ring group, a tetrazolium ring group, a thiadiazolium ring group, a pyridinium ring group, a pyrimidinium ring group, and a triazinium ring group. Thereamong, preferable is a triazolium ring group (for example, a 1,2,4-triazolium-3-thiolate ring group). As the aryl group, mentioned is a phenyl group or a naphthyl group. As the alkyl group, mentioned is a straight, branched, or cyclic alkyl group having from 1 to 30 carbon atoms. When the mercapto group forms a salt, examples of counter ions include a cation ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Zn}^{2+}$  or the like) of an alkaline metal, an alkaline earth metal, a heavy metal or the like, an ammonium ion, a heterocyclic group having a quaternized nitrogen atom, and a phosphonium ion.

[0220]

The mercapto group as an adsorptive group may further be tautomerized to be a thione group. Specifically mentioned are a thioamide group (a  $\text{-C(=S)-NH-}$  group on this occasion), and a group which has a partial structure of the thioamido group, namely, a chained or cyclic thiamide group, a thioamido group, a thiourethane group, or a dithiocarbamic ester group. Examples of such cyclic groups include a thiazolidine-2-thione group, an oxazolidine-2-thione group, a 2-thiohydantoin group, a rhodanine group, an isorhodanine group, a thiobarbituric acid group, and a 2-thioxo-oxazolidin-4-one group.

Examples of the thione groups as the adsorptive group include not only a thione group generated by tautomerizing the above-described mercapto group, but also a chained or cyclic thioamide group, thioureido group, thiourethane group and dithiocarbamic acid ester group which can not be tautomerized to the mercapto group (having no hydrogen atom at an  $\alpha$ -position of the thione group).

[0221]

The heterocyclic group having at least one atom selected from the group consisting of: a nitrogen atom, a sulfur atom, a selenium atom and a tellurium atom as an adsorptive group denotes a nitrogen-containing heterocyclic group having an  $\text{-NH-}$  group which can form an imino silver ( $>\text{NAg}$ ) as a partial structure



of the heterocycle, or a heterocyclic group, having an -S- group, an -Se- group, a -Te- group, or an =N- group as a partial structure of a heterocycle, which can be bonded to a silver ion by a coordinate bond; examples of the former include a benzotriazole group, a triazole group, an indazole group, a pyrazole group, a tetrazole group, a benzimidazole group, an imidazole group, and a purine group; examples of the latter include a thiophene group, a thiazole group, an oxazole group, a benzothiazole group, a benzoxazole group, a thiadiazole group, an oxadiazole group, a triazine group, a selenazole group, a benzoselenazole group, a tellurazole group, and a benzotellurazole group. The former is preferable.

[0222]

The sulfide group or the disulfide group as an adsorptive group denotes all of groups which each have an -S- group or an -S-S- group as a partial structure and preferably groups having a partial structure of alkyl (or alkylene)-X-alkyl (or alkylene), aryl (or arylene)-X-alkyl (or alkylene), or aryl (or arylene)-X-aryl (or arylene), wherein X represents a -S- group or a -S-S group. Further, the sulfide group or the disulfide group may form a ring structure. When the cyclic structure is formed, specifically mentioned is a group containing, for example, a thiolanering, a 1,3-dithiolanering, a 1,2-dithiolane ring, a thiane ring, a dithiane ring, or a

thiomorpholine ring. The sulfide group is particularly preferably a group having a partial structure of alkyl-(or alkylene)-S-alkyl (or alkylene). The disulfide group is particularly preferably a 1,2-dithiolane ring-containing group.

[0223]

The cationic group as an adsorptive group means a group having a quaternized nitrogen atom and, specifically, refers to a group containing an ammonio group or a nitrogen-containing heterocyclic group having a quaternized nitrogen atom. The ammonio group refers to a trialkylammonio group, a dialkylarylammonio group, an alkyl diarylammonio group or the like; examples of such ammonio groups include a benzyldimethylammonio group, a trihexylammonio group, and a phenyldiethylammonio group. As for the nitrogen-containing heterocyclic group having a quaternized nitrogen atom, mentioned are, for example, a pyridinio group, a quinolinio group, an isoquinolinio group, and an imidazolio group, in which a pyridinio group and an imidazolio group are preferable and a pyridinio group is particularly preferable. Any one of these nitrogen-containing heterocyclic groups each having a quaternized nitrogen atom may have a given substituent. However, when it refers to a pyridinio group or an imidazolio group, the substituent is preferably an alkyl group, an aryl group,

an acylamino group, a chlorine atom, an alkoxycarbonyl group, or a carbamoyl group. When it refers to a pyridinio group, the substituent is particularly preferably a phenyl group.

The ethynyl group as an adsorptive group means a  $-C\equiv CH$  group in which a hydrogen atom may be substituted.

[0224]

The above-described adsorptive groups may each have a given substituent. Examples of substituents include a halogen atom (a fluorine atom, a chlorine atom, a bromine atom, or an iodine atom), an alkyl group (inclusive of a straight-chain, branched-chain, or cyclic alkyl group inclusive of a bicycloalkyl group and an active methine group), an alkenyl group, an alkynyl group, an aryl group, a heterocyclic group (a position to be substituted is not limited), an acyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a heterocycloxy carbonyl group, a carbamoyl group, an N-hydroxycarbamoyl group, an N-acylcarbamoyl group, an N-sulfonylcarbamoyl group, an N-carbamoylcarbamoyl group, a thiocarbamoyl group, an N-sulfamoylcarbamoyl group, a carbazoyl group, a carboxyl group or a salt thereof, an oxalyl group, an oxamoyl group, a cyano group, a carbonimidoyl group, a formyl group, a hydroxyl group, an alkoxy group (inclusive of a group having a recurring unit of an ethyleneoxy group or a propyleneoxy group), an aryloxy group, a heterocycloxy group,

an acyloxy group, an (alkoxy or aryloxy) carbonyloxy group, a carbamoyloxy group, a sufonyloxy group, an amino group, (an alkyl, aryl, or a heterocycle) amino group, an acylamino group, a sulfonamide group, a ureido group, a thioureido group, an imido group, an (alkoxy or aryloxy) carbonylamino group, a sufamoylamino group, a semicarbazide group, a thiosemicarbazide group, a hydrazino group, an ammonio group, an oxamoylamino group, an N-(alkyl or aryl) sufonylureido group, an N-acylureido group, an N-acylsulfamoylamino group, a hydroxyamino group, a nitro group, a heterocyclic group having a quaternized nitrogen atom (for example, a pyridinio group, an imidazolio group, a quinolinio group, or an isoquinolinio group), an isocyano group, an imino group, a mercapto group, (an alkyl, aryl, or a heterocycle) thio group, (an alkyl, aryl, or a heterocycle) dithio group, an (alkyl or aryl) sulfonyl group, an (alkyl or aryl) sulfinyl group, a sulfo group or a salt thereof, a sulfamoyl group, an N-acylsulfamoyl group, an N-sulfonylsulfamoyl group or a salt thereof, a phosphino group, a phosphinyl group, a phosphinyloxy group, a phosphinylamino group, and a silyl group. Further, the term "active methine" as used herein is intended to mean a methine group substituted by two electron-attracting groups; the term "electron-attracting group" as used herein is intended to mean an acyl group, an alkoxycarbonyl group, an aryloxy carbonyl group, a carbamoyl group, an alkylsulfonyl group, an arylsulfonyl group,

a sufamoyl group, a trifluoromethyl group, a cyano group, a nitro group, or a carbonimidoyl group. Two electron-attacking groups may be combined with each other to form a cyclic configuration. Further, the term "salt" as used herein is intended to mean a cation of, for example, an alkaline metal, an alkaline earth metal, or a heavy metal, or an organic cation such as an ammonium ion, and a phosphonium ion.

[0225]

Specific examples of the adsorptive groups further include those as described in JP-A No. 11-95355, pp. 4 to 7.

[0226]

In the formula (I), the adsorptive group represented by A is more preferably a mercapto-substituted heterocyclic group (for example, a 2-mercaptothiadiazole group, a 3-mercapto-1,2,4-triazole group, a 5-mercaptotetrazole group, a 2-mercapto-1,3,4-oxadiazole group, a 2-mercaptobenzthiazole group, a 2-mercaptobenzimidazole, 1,5-dimethyl-1,2,4-triazolium-3-thiolate group), a dimercapto-substituted heterocyclic group (for example, a 2,4-dimercaptopyrimidine group, a 2,4-dimercaptotriazine group, a 3,5-dimercapto-1,2,4-triazole group, a 2,5-dimercapto-1,3-thiazole group), or a nitrogen-containing heterocyclic group having an -NH- group which can form an imino

silver (>NAg) as a partial structure of a heterocycle (for example, a benzotriazole group, a benzimidazole group, or an indazole group). The dimercapto-substituted heterocyclic group is particularly preferable.

[0227]

In the formula (I), W represents a divalent linking group. The linking group may be any linking group so long as it does not give any detrimental effect to photographic characteristics. For example, any divalent linking group constituted by a carbon atom, a hydrogen atom, an oxygen atom, a nitrogen atom, or a sulfur atom can be utilized. Examples of such linking groups include an alkylene group having from 1 to 20 carbon atoms (for example, a methylene group, an ethylene group, a trimethylene group, a tetramethylene group, or a hexamethylene group), an alkenylene group having from 2 to 20 carbon atoms, an alkynylene group having from 2 to 20 carbon atoms, an arylene group having from 6 to 20 carbon atoms (for example, a phenylene group, or a naphthylene group), a -CO- group, an -SO<sub>2</sub>- group, an -O- group, an -S- group, an -NR<sub>1</sub>- group and combinations thereof, in which R<sub>1</sub> represents a hydrogen atom, an alkyl group, a heterocyclic group, or an aryl group. An aliphatic group represented by R<sub>1</sub> is preferably an alkyl group, an alkenyl group or an aralkyl group which is straight, branched or cyclic and has 1 to 30, particularly 1 to 20 carbon atoms (such as a methyl group, an

ethyl group, an isopropyl group, a t-butyl group, an n-octyl group, an n-decyl group, an n-hexadecyl group, a cyclopropyl group, a cyclopentyl group, a cyclohexyl group, an allyl group, a 2-butenyl group, a 3-pentenyl group, a propargyl group, a 3-pentynyl group or a benzyl group). An aryl group represented by  $R_1$  is preferably a monocyclic or condensed aryl group having 6 to 30, more preferably having 6 to 20 carbon atoms, and examples of the aryl group include a phenyl group or a naphthyl group. The linking group represented by W may have a given substituent. This given substituent is similar to the above-described substituent of the adsorptive group.

[0228]

In the formula (I), the reducing group represented by B denotes a silver ion-reducible group; examples of such reducing groups include a formyl group, an amino group, a group having a triple bond such as an acetylene group or a propargyl group, a mercapto group, a residue derived from a compound selected from hydroxylamines, hydroxamic acids, hydroxyureas, hydroxyurethanes, hydroxysemicarbazides, reductones (inclusive of derivatives thereof), anilines, phenols (inclusive of chroman-6-ols, 2,3-dihydrobenzofuran-5-ols, aminophenols, sulfonamidophenols, hydroquinones, catechols, resorcinols, benzene triols, and polyphenols such as bisphenols), hydrazines, hydrazides, and phenidones. It goes

without saying that these reducing groups may each individually have a given substituent.

[0229]

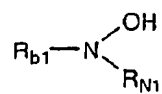
In the formula (I), preferable examples of the reducing groups represented by B include residues derived from compounds represented by the following formulas B<sub>1</sub> to B<sub>13</sub>:

[0230]

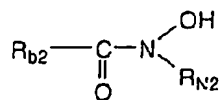
[Formula 37]



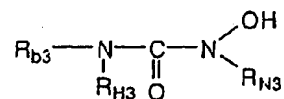
(B<sub>1</sub>)



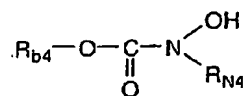
(B<sub>2</sub>)



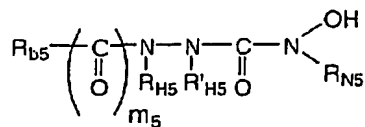
(B<sub>3</sub>)



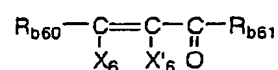
(B<sub>4</sub>)



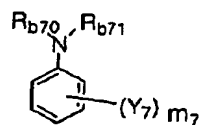
(B<sub>5</sub>)



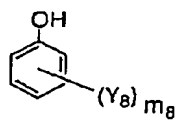
(B<sub>6</sub>)



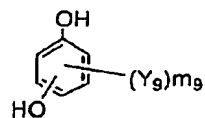
(B<sub>7</sub>)



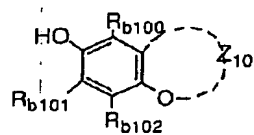
(B<sub>8</sub>)



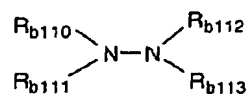
(B<sub>9</sub>)



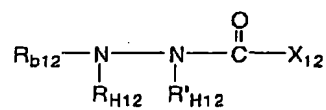
(B<sub>10</sub>)



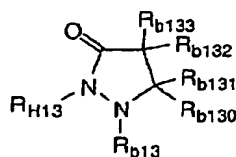
(B<sub>11</sub>)



(B<sub>12</sub>)



(B<sub>13</sub>)



[0231]

In the formulas (B<sub>1</sub>) to (B<sub>13</sub>), R<sub>b1</sub>, R<sub>b2</sub>, R<sub>b3</sub>, R<sub>b4</sub>, R<sub>b5</sub>, R<sub>b70</sub>, R<sub>b71</sub>, R<sub>b110</sub>, R<sub>b111</sub>, R<sub>b112</sub>, R<sub>b113</sub>, R<sub>b12</sub>, R<sub>b13</sub>, R<sub>N1</sub>, R<sub>N2</sub>, R<sub>N3</sub>, R<sub>N4</sub>, R<sub>N5</sub> each independently represent a hydrogen atom, an alkyl group, an aryl group, or a heterocyclic group; R<sub>H3</sub>, R<sub>H5</sub>, R'<sub>H5</sub>, R<sub>H12</sub>, R'<sub>H12</sub>, R<sub>H13</sub> each individually represent a hydrogen atom, an alkyl group, an aryl group, an acyl group, an alkylsulfonyl group, or arylsulfonyl group, in which R<sub>H3</sub> may further be a hydroxyl group; R<sub>b100</sub>, R<sub>b101</sub>, R<sub>b102</sub>, R<sub>b130</sub> to R<sub>b133</sub> each individually represent a hydrogen atom or a substituent; Y<sub>7</sub> and Y<sub>8</sub> each individually represent a substituent exclusive of a hydroxyl group; Y<sub>9</sub> represents a substituent; m<sub>5</sub> represents an integer of 0 or 1; m<sub>7</sub> represents an integer of from 0 to 5; m<sub>8</sub> represents an integer of from 1 to 5; m<sub>9</sub> represents an integer of from 0 to 4; Y<sub>7</sub>, Y<sub>8</sub>, and Y<sub>9</sub> may each individually further be an aryl group which is condensed to a benzene ring (benzene condensed ring) and such benzene condensed ring may have a substituent; Z<sub>10</sub> represents a non-metallic atomic group capable of forming a ring; X<sub>12</sub> represents a hydrogen atom, an alkyl group, an aryl group, a heterocyclic group, an alkoxy group, an amino group (inclusive of an alkylamino group, an arylamino group, a heterocycloaminogroup, and a cyclic aminogroup), or a carbamoyl group.

In the formula (B<sub>6</sub>), X<sub>6</sub>, and X'<sub>6</sub> each individually represent a hydroxyl group, an alkoxy group, a mercapto group, an alkylthio

group, an amino group (inclusive of an alkylamino group, an arylamino group, a heterocycloamino group, and a cyclic amino group), an acylamino group, a sulfonamide group, an alkoxycarbonylamino group, a ureido group, an acyloxy group, an acylthio group, an alkylaminocarbonyloxy group, and an arylaminocarbonylox group;  $R_{b60}$  and  $R_{b61}$  each individually represent an alkyl group, an aryl group, an amino group, an alkoxy group, and aryloxy group, in which  $R_{b60}$  and  $R_{b61}$  may be combined with each other to form a cyclic structure.

[0232]

The term "alkyl group" as used in the above description of each group of the formulas  $(B_1)$  to  $(B_{13})$  is intended to include a straight, branched or cyclic, substituted or unsubstituted alkyl group having from 1 to 30 carbon atoms; the term "aryl group" is intended to include a monocyclic or condensed cyclic, substituted or unsubstituted aromatic hydrocarbon cycle such as a phenyl group or a naphthyl group; and the term "heterocyclic group" is intended to include an aromatic or non-aromatic, monocyclic or condensed cyclic, substituted or unsubstituted heterocyclic group having at least one heteroatom.

Further, the term "substituent" as used in the above description of respective groups represented by the formulas  $(B_1)$  to  $(B_{13})$  is intended to include same substituents as those of the above-described adsorptive group. The substituents may

each individually be further substituted by any one of these substituents.

[0233]

In the formulas (B<sub>1</sub>) to (B<sub>5</sub>), R<sub>N1</sub>, R<sub>N2</sub>, R<sub>N3</sub>, R<sub>N4</sub>, and R<sub>N5</sub> represent each individually preferably a hydrogen atom or an alkyl group. The alkyl group is preferably a straight, branched, or cyclic, substituted or unsubstituted alkyl group having from 1 to 12 carbon atoms, and more preferably a straight, branched, substituted or unsubstituted alkyl group having from 1 to 6 carbon atoms such as a methyl group, an ethyl group, a propyl group or a benzyl group.

In the formula (B<sub>1</sub>), R<sub>b1</sub> preferably represents an alkyl group or a heterocyclic group. The alkyl group is a straight, branched or cyclic, substituted or unsubstituted alkyl group having preferably from 1 to 30 carbon atoms, and more preferably from 1 to 18 carbon atoms; and the heterocyclic group is a 5- or 6-membered, monocyclic or condensed cyclic, aromatic or non-aromatic heterocyclic group and may have a substituent. The heterocyclic group is preferably an aromatic heterocyclic group; examples of such aromatic heterocyclic groups include a pyridine ring group, a pyrimidine ring group, a triazine ring group, a thiazole ring group, a benzothiazole ring group, an oxazole ring group, a benzoxazole ring group, an imidazole ring group, a benzimidazole ring group, a pyrazole ring group, an

indazole ring group, an indole ring group, a purine ring group, a quinoline ring group, an isoquinoline ring group, and a quinazoline ring group, and particularly preferably a triazine ring group, and a benzothiazole ring group. It is also a preferable example of the compound represented by the formula (B<sub>1</sub>) that the alkyl group or the heterocyclic group represented by R<sub>b1</sub> further has one or two -N(R<sub>N1</sub>)OH groups as substituents.

[0234]

In the formula (B<sub>2</sub>), R<sub>b2</sub> preferably represents an alkyl group, an aryl group or a heterocyclic group, and more preferably represents an alkyl group or an aryl group. Preferable ranges of such alkyl groups are same as those as described in R<sub>b1</sub>. The aryl group is preferably a phenyl group or a naphthyl group, and particularly preferably a phenyl group and may have a substituent. It is also a preferable example of the compound represented by the formula (B<sub>2</sub>) that the group represented by R<sub>b2</sub> further has one or two -CON(R<sub>N2</sub>)OH groups as substituents. In the formula (B<sub>3</sub>), R<sub>b3</sub> preferably represents an alkyl group or an aryl group. Preferable ranges of these groups are same as those as described in R<sub>b1</sub> and R<sub>b2</sub>. R<sub>H3</sub> preferably represents a hydrogen atom, an alkyl group or a hydroxyl group, and more preferably represents a hydrogen atom. It is also a preferable example of the compound represented by the formula (B<sub>3</sub>) that the group represented by R<sub>b3</sub> further has one or two

$-N(R_{H3})CON(R_{N3})OH$  groups as substituents. Further,  $R_{b3}$  and  $R_{N3}$  may be combined with each other to form a ring structure (preferably 5- or 6-membered saturated heterocycle).

[0235]

In the formula  $(B_4)$ ,  $R_{b4}$  preferably represents an alkyl group. A preferable range thereof is same as that as described in  $R_{b1}$ . It is also a preferable example of the compound represented by the formula  $(B_4)$  that the group represented by  $R_{b4}$  further has one or two  $-OCON(R_{N4})OH$  groups as substituents.

In the formula  $(B_5)$ ,  $R_{b5}$  preferably represents an alkyl group or an aryl group, and more preferably an aryl group. Preferable ranges of these groups are same as those as described in  $R_{b1}$  and  $R_{b2}$ .  $R_{H5}$  and  $R'_{H5}$  each preferably represent a hydrogen atom or an alkyl group, and more preferably represent a hydrogen atom.

[0236]

In the formula  $(B_6)$ ,  $R_{b60}$  and  $R_{b61}$  are preferably combined with each other to form a ring structure. The thus-formed ring structure may be a 5- to 7-membered non-aromatic carbocycle or heterocycle and may be a monocycle or a condensed ring. Specific examples of preferable ring structures include a 2-cyclopenten-1-one ring, a 2,5-dihydrofuran-2-one ring, a 3-pyrrolin-2-one ring, a 4-pyrazolin-3-one ring, a

2-cyclohexen-1-one ring, a 5,6-dihydro-2H-pyran-2-one ring, a 5,6-dihydro-2-pyridone ring, a 1,2-dihydronaphthalen-2-one ring, a coumarin ring (benzo- $\alpha$ -pyran-2-one ring), a 2-quinolone ring, a 1,4-dihydronaphthalen-1-one ring, a chromone ring (benzo- $\gamma$ -pyran-4-one ring), a 4-quinolone ring, an inden-1-one ring, a 3-pyrroline-2,4-dione ring, a uracil ring, a thiouracil ring and a dithiouracil ring, and more preferable are a 2-cyclopenten-1-one ring, a 2,5-dihydrofuran-2-one ring, a 3-pyrrolin-2-one ring, a 4-pyrazolin-3-one ring, a 1,2-dihydronaphthalen-2-one ring, a coumarin ring (benzo- $\alpha$ -pyran-2-one ring), a 2-quinolone ring, a 1,4-dihydronaphthalen-1-one ring, a chromone ring (benzo- $\gamma$ -pyran-4-one ring), a 4-quinolone ring, an inden-1-one ring, and a dithiouracil ring, and still more preferable are a 2-cyclopenten-1-one ring, a 2,5-dihydrofuran-2-one ring, a 3-pyrrolin-2-one ring, an inden-1-one ring, and a 4-pyrazolin-3-one ring.

[0237]

When  $X_6$  and  $X'_6$  each individually represent a cyclic amino group, the term "cyclic amino group" as used in the above description is intended to include a non-aromatic nitrogen-containing heterocyclic group formed by combining with a nitrogen atom; examples of such cyclic amino groups include a pyrrolidino group, a piperidino group, a piperazino

group, a morpholino group, a 1,4-thiazin-4-yl group, a 2,3,5,6-tetrahydro-1,4-thiazin-4-yl group, and an indolyl group.

$X_6$ , and  $X'_6$  each individually represent preferably a hydroxyl group, a mercapto group, an amino group (inclusive of an alkylamino group, an arylamino group or a cyclic amino group), an acylamino group, a sulfonamide group, an acyloxy group, or an acylthio group, more preferably a hydroxyl group, a mercapto group, an amino group, an alkylamino group, a cyclic amino group, a sulfonamide group, an acylamino group, or an acyloxy group, and particularly preferably a hydroxyl group, an amino group, an alkylamino group, or a cyclic amino group. Further, at least one of  $X_6$  and  $X'_6$  preferably represents a hydroxyl group.

[0238]

In the formula ( $B_7$ ),  $R_{b70}$  and  $R_{b71}$  each individually preferably represent a hydrogen atom, an alkyl group or an aryl group, and more preferably an alkyl group. A preferable range of the alkyl group is same as that as described in  $R_{b1}$ .  $R_{b70}$  and  $R_{b71}$  may be combined with each other to form a ring structure (for example, a pyrrolidine ring, a piperidine ring, a morpholino ring, or a thiomorpholino ring). Examples of preferable substituents represented by  $Y_7$  include an alkyl group (a preferable range thereof is same as that as described in  $R_{b1}$ ),



an alkoxy group, an amino group, an acylamino group, a sulfonamide group, a ureido group, an acyl group, an alkoxy carbonyl group, a carbamoyl group, a sulfamoyl group, a chlorine atom, a sulfo group and a salt thereof, a carboxyl group and a salt thereof.  $m_7$  preferably represents 0 to 2.

[0239]

In the formula ( $B_8$ ),  $m$  preferably represents 1 to 4 and a plurality of  $Y_8$ 's may be same with or different from one another.  $Y_8$  at the time of  $m_8$  representing 1 or at least one of a plurality of  $Y_8$ 's at the time of  $m_8$  representing 2 or more is preferably an amino group (inclusive of an alkylamino group or an arylamino group), a sulfonamide group, or an acylamino group. When  $m_8$  represents 2 or more, remaining  $Y_8$ 's are each individually preferably represent a sulfonamide group, an acylamino group, a ureido group, an alkyl group, an alkylthio group, an acyl group, an alkoxy carbonyl group, a carbamoyl group, a sulfo group and a salt thereof, a carboxyl group and a salt thereof, or a chlorine atom. As for substituents represented by  $Y_8$ , when an o'- (or p'-) hydroxyphenylmethyl group (permissible to further have a substituent) is substituted at an ortho position or a para position of a hydroxyl group, they denote a group of compounds ordinarily called as bisphenols; this case is also a preferable example of the compound represented by the formula ( $B_8$ ). Further, it is also extremely preferable that  $Y_8$

represents a benzene condensed ring and, as a result, the formula (B<sub>8</sub>) represents naphthols.

[0240]

In the formula (B<sub>9</sub>), substitution sites of two hydroxyl groups may each be at an ortho position (catechols), a meta position (resorcinols), or a para position (hydroquinones). m, preferably represents 1 or 2 and, when Y, exists in a plural number, they may be same with or different from one another. Preferable examples of substituents represented by Y, include a chlorine atom, an acylamino group, a ureido group, a sulfonamide group, an alkyl group, an alkylthio group, an alkoxy group, an acyl group, an alkoxycarbonyl group, a carbamoyl group, a sulfo group and a salt thereof, a carboxyl group and a salt thereof, a hydroxyl group, an alkylsulfonyl group, and an arylsulfonyl group. Further, it is also preferable that Y, represents a benzene condensed ring and, as a result, the formula (B<sub>9</sub>) represents 1,4-naphthohydroquinones. When the formula (B<sub>9</sub>) represents catechols, Y, particularly preferably represents a sulfo group or a salt thereof, or a hydroxyl group.

[0241]

In the formula (B<sub>10</sub>), when R<sub>b100</sub>, R<sub>b101</sub>, and R<sub>b102</sub> represent substituents, preferable examples of the substituents represented by R<sub>b100</sub>, R<sub>b101</sub>, and R<sub>b102</sub> are same as the preferable

examples of the substituents represented by Y<sub>9</sub>, in which an alkyl group (particularly a methyl group) is preferable. A ring structure formed by Z<sub>10</sub> is preferably a coumarone ring or a 2,3-dihydrobenzofuran ring. These ring structures may each have a substituent and may each form a spiro ring.

[0242]

In the formula (B<sub>11</sub>), R<sub>b110</sub>, R<sub>b111</sub>, R<sub>b112</sub>, R<sub>b113</sub> each individually preferably represent an alkyl group, an aryl group or a heterocyclic group. Preferable ranges thereof are same as those as described in R<sub>b1</sub> and R<sub>b2</sub> and, among other things, an alkyl group is preferable. Further, two alkyl groups among groups represented by R<sub>b110</sub> to R<sub>b113</sub> may be combined with each other to form a ring structure. The term "ring structure" as used in the above description is intended to include a 5- or 6-membered non-aromatic heterocycle; examples of such heterocycles include a pyrrolidine ring, a piperidine ring, a morpholine ring, a thiomorpholine ring, and a hexahydropyridazine ring. In the formula (B<sub>12</sub>), R<sub>b12</sub> preferably represents an alkyl group, an aryl group or a heterocyclic group. A preferable range thereof is same as that as described in each of R<sub>b1</sub> and R<sub>b2</sub>. X<sub>12</sub> preferably represents an alkyl group, an aryl group (particularly a phenyl group), a heterocyclic group, an alkoxy group, an amino group (inclusive of an alkylamino group, an arylamino group, a heterocycloamino group, and a cyclic

amino group), or a carbamoyl group, in which an alkyl group (particularly preferably an alkyl group having from 1 to 8 carbon atoms), an aryl group (particularly preferably a phenyl group), an amino group (particularly preferably an alkylamino group, an arylamino group, or a cyclic amino group) are more preferable.  $R_{H12}$  and  $R'_{H12}$  each individually preferably represent a hydrogen atom or an alkyl group, and more preferably represent a hydrogen atom.

[0243]

In the formula (B<sub>13</sub>),  $R_{b13}$  preferably represent an alkyl group or an aryl group. A preferable range thereof is same as that as described in each of  $R_{b1}$  and  $R_{b2}$ .  $R_{b130}$ ,  $R_{b131}$ ,  $R_{b132}$ , and  $R_{b133}$ , each individually preferably represent a hydrogen atom, an alkyl group (particularly preferably having from 1 to 8 carbon atoms), or an aryl group (particularly a phenyl group).  $R_{H13}$  is preferably a hydrogen atom or an acyl group, and more preferably a hydrogen atom.

[0244]

In the formula (I), the reducing group represented by B is preferably selected from hydroxylamines, hydroxamic acids, hydroxyureas, hydroxysemicarbazides, phenols, hydrazines, hydrazides, and phenidones. Hydroxyureas, hydroxysemicarbazides, phenols, hydrazides, and phenidones are

particularly preferable.

[0245]

An oxidation potential of a reducing group represented by B in the formula (I) can be measured by a method described in, for example, Akira Fujishima, "Electrochemical Measurement Method", pp. 150-208, (published by Gihodo Co., Ltd.), or "Experiment Chemistry Lecture", 4th ed., vol. 9, pp. 282-344, (compiled and edited by The Chemical Society of Japan; published by Maruzen Co., Ltd.). For example, a rotating disc voltammetry technique can be utilized. Specifically, a sample is dissolved in a solution having a mixing ratio of 10%:90% by volume of methanol to a Britton-Robinson buffer solution at pH 6.5. After being aerated with a nitrogen gas for 10 minutes, the resultant solution is subjected to measurements with a sweep speed of 20 mV/second at 1000 rotations/minute at 25°C by using a rotating disc electrode (RDE) made of glassy carbon as a working electrode, a platinum wire as a counter electrode, and a saturated calomel electrode as a reference electrode, thereby constructing a voltamogram. A half-wave potential ( $E_{1/2}$ ) can be obtained from the thus-constructed voltamogram.

When the reducing group represented by B according to the invention is subjected to measurements by the above-described measuring method, the oxidation potential thereof is preferably in a range from approximately -0.3 V to

approximately 1.0 V, more preferably from approximately -0.1 V to approximately 0.8 V, and particularly preferably from approximately 0 V to approximately 0.7 V.

[0246]

Many of the compounds used as the redicuing group represented by B according to the invention are well known in the photographic industry, and examples thereof are described in JP-A Nox. 2001-42466, 8-114884, 8-314051, 8-333325, 9-133983, 11-282117, 10-246931, 10-90819, 9-54384, 10-171060 and 7-77783. Further, the compound described in USP No. 6,054,260 is also an example of the phenols.

[0247]

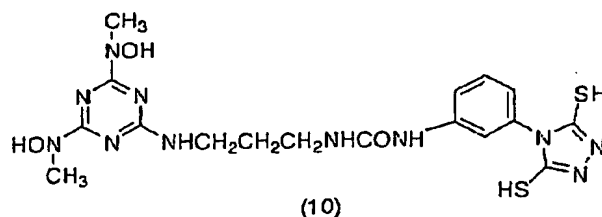
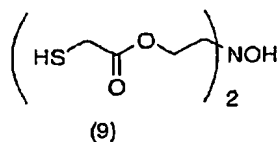
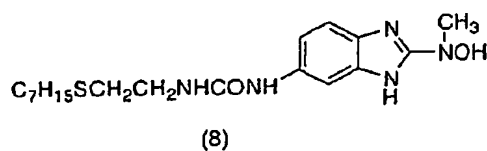
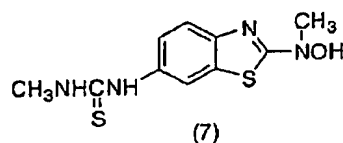
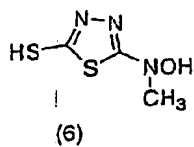
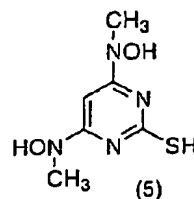
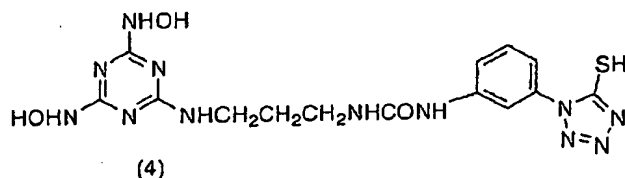
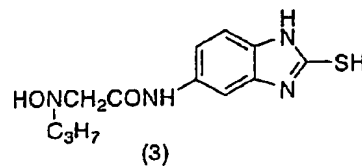
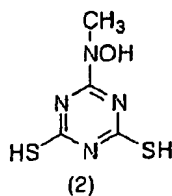
The compound represented by the formula (I) according to the invention may be such that a ballast group or a polymer chain that is commonly used in an immobile additive for photographic use such as a coupler is incorporated thereinto. As for polymers, mentioned are those as described in, for example, JP-A No. 1-100530.

[0248]

The compound represented by the formula (I) according to the invention may either be a bis-form or a tris-form. A molecular weight of the compound represented by the formula

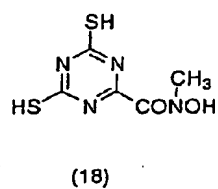
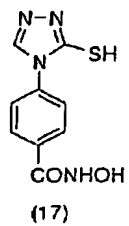
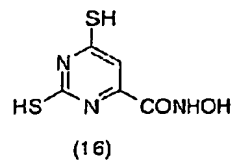
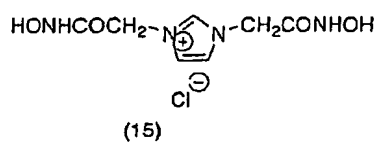
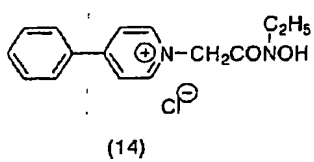
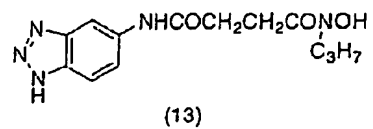
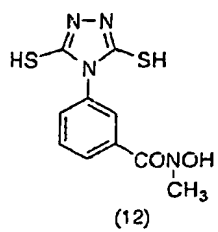
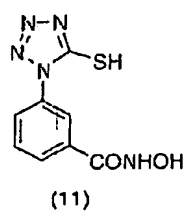
[ 0 2 4 9 ]

[ 0 2 5 0 ]

Nc1nc(N)nc(N)c1S  
(1)

[0251]

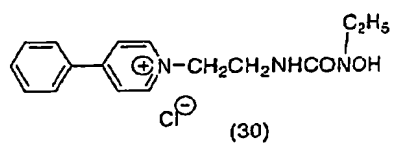
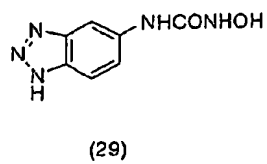
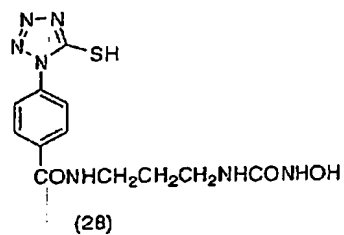
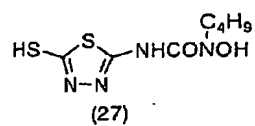
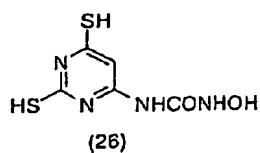
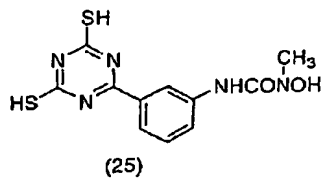
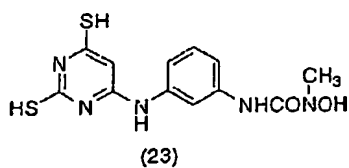
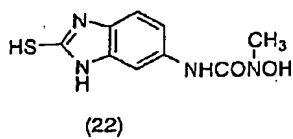
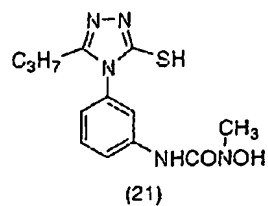
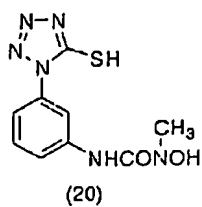
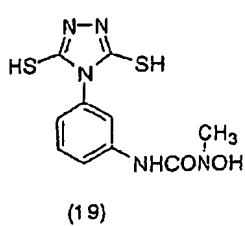
[Formula 39]





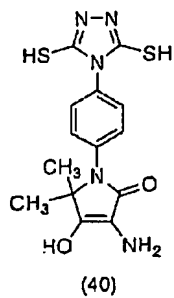
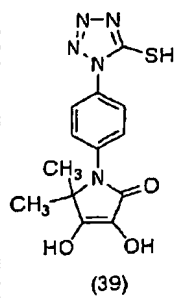
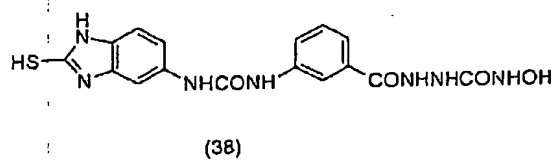
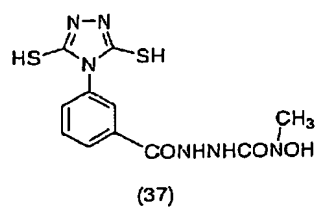
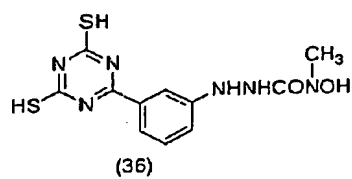
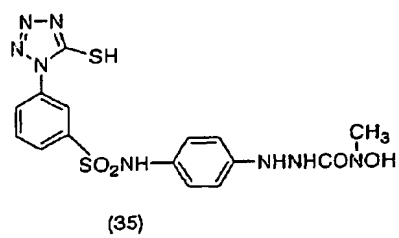
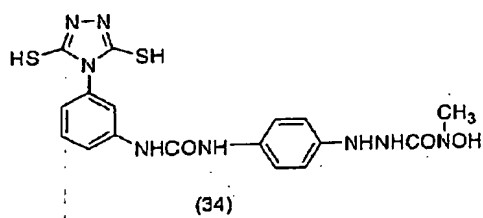
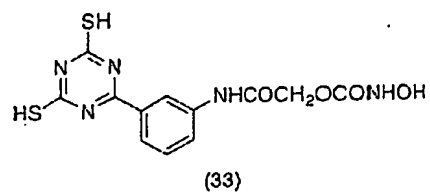
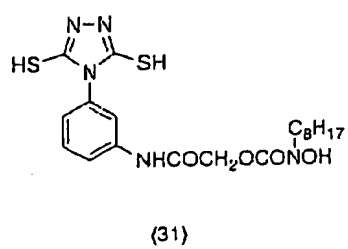
[0252]

[Formula 40]



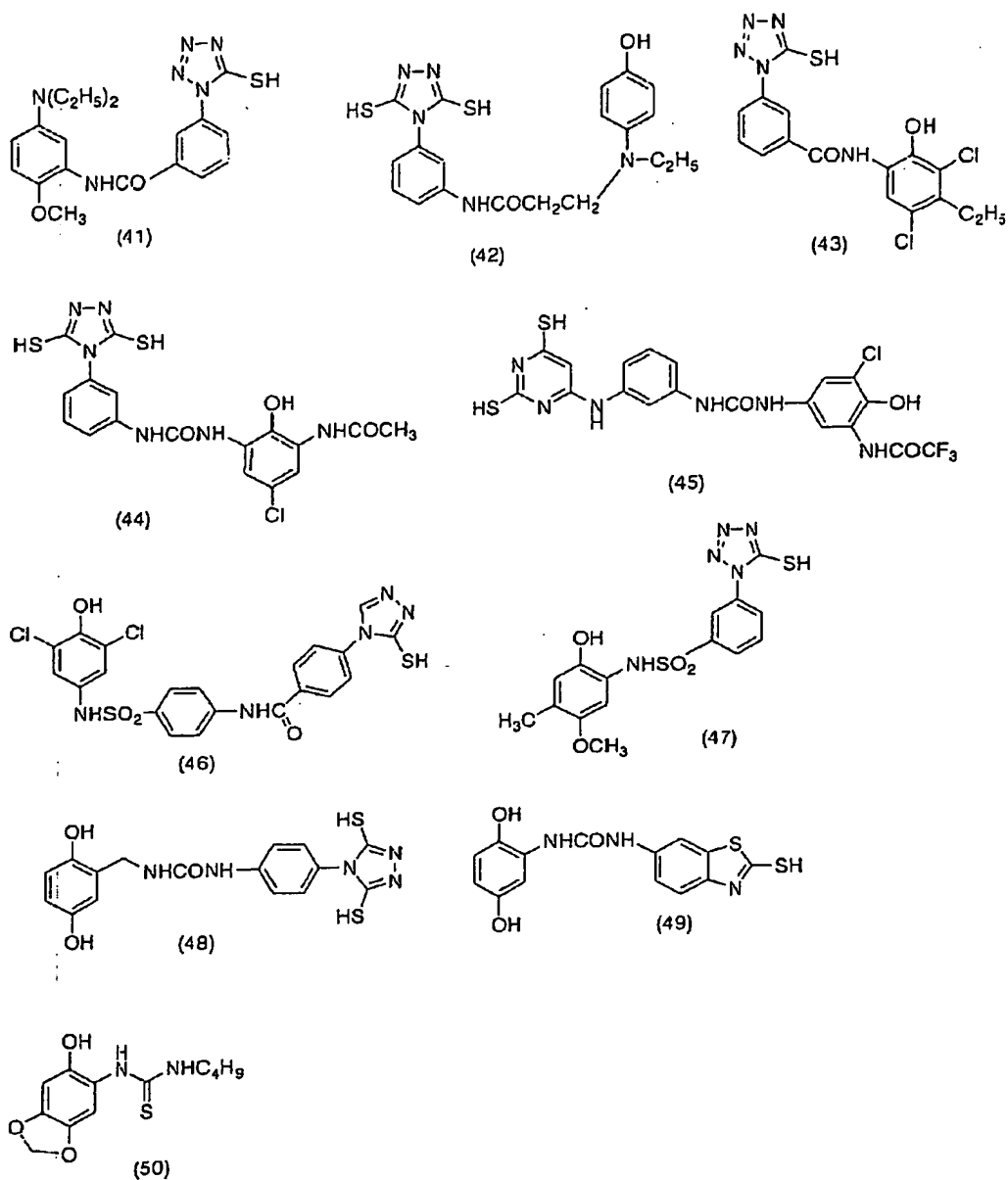
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[Formula 41]



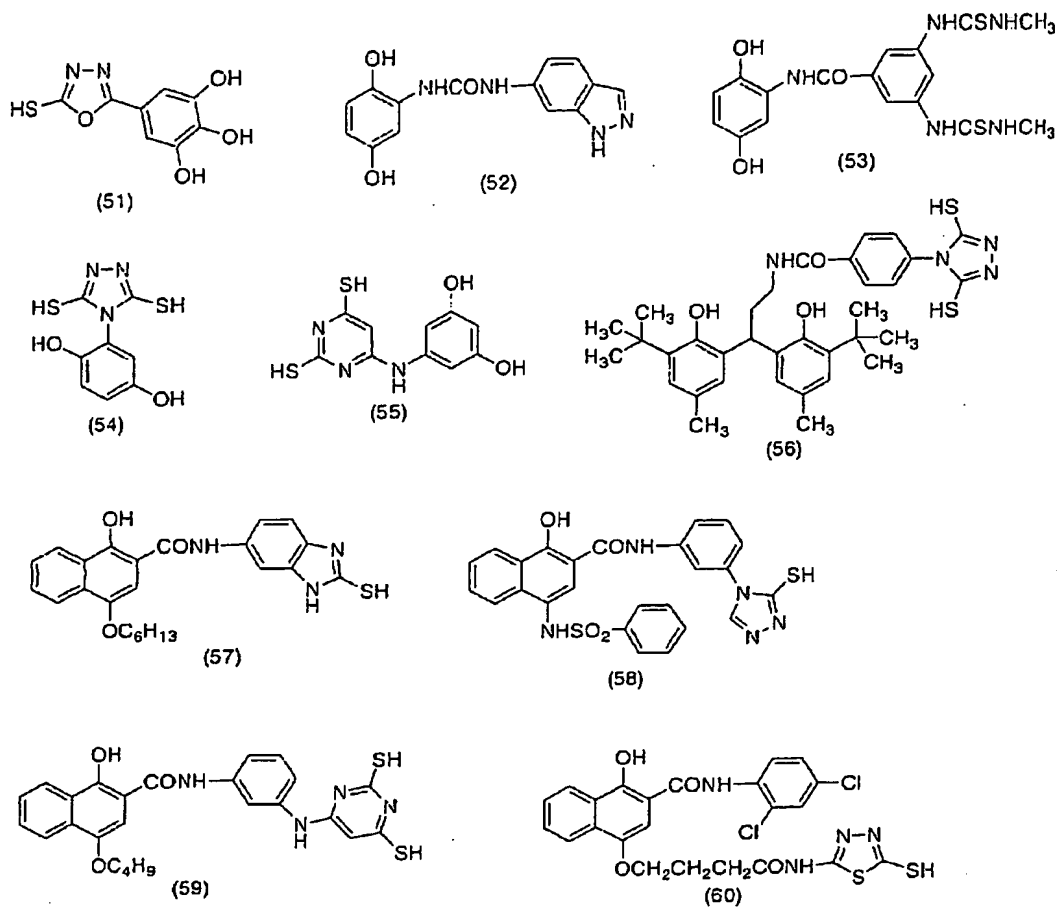
[0254]

[Formula 42]



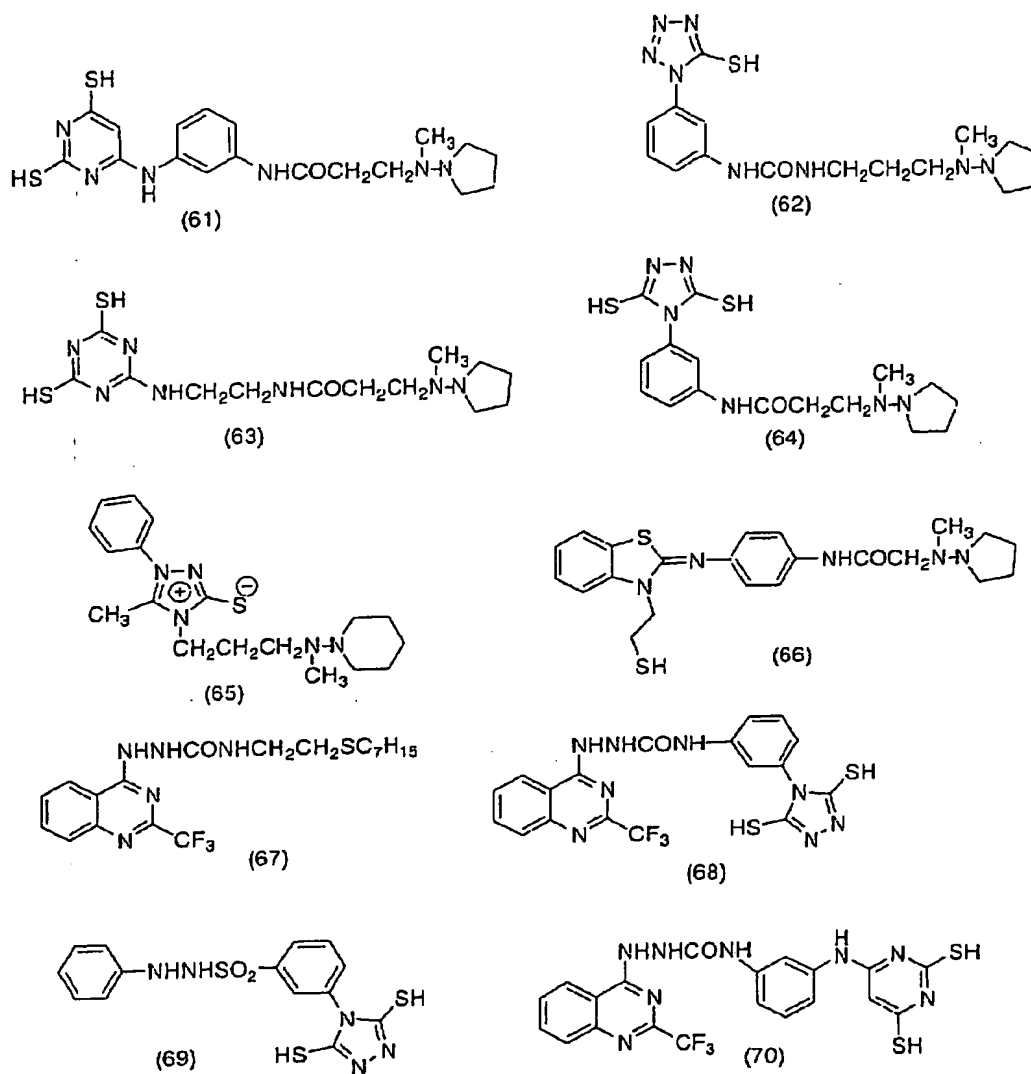
[0255]

[Formula 43]



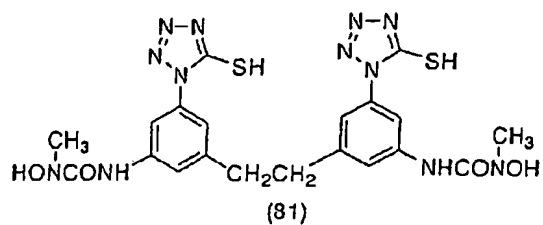
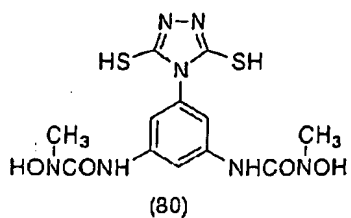
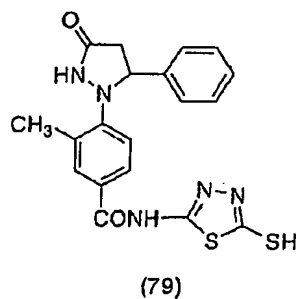
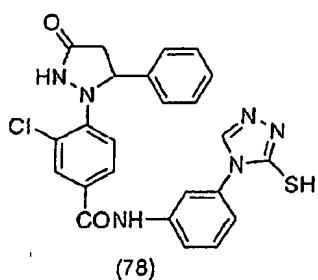
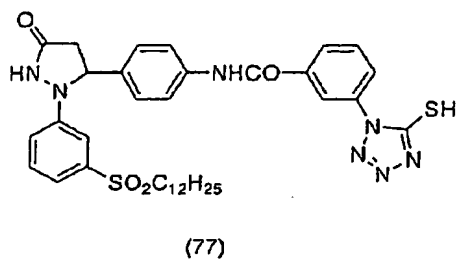
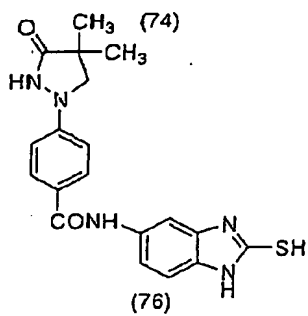
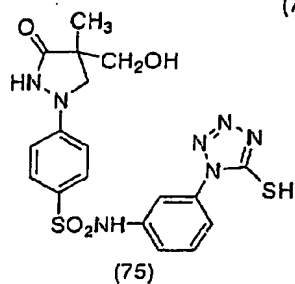
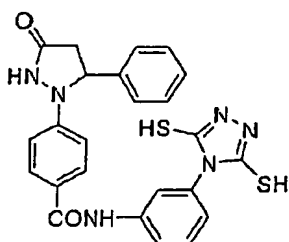
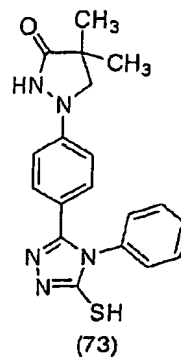
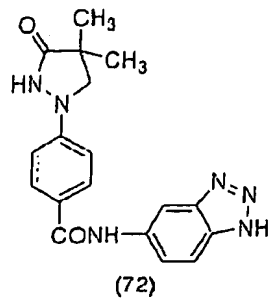
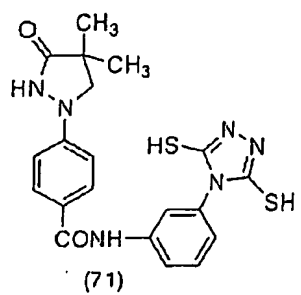
[0256]

[Formula 44]



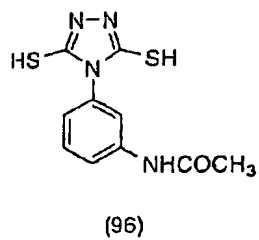
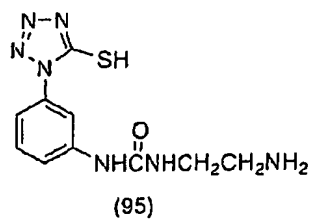
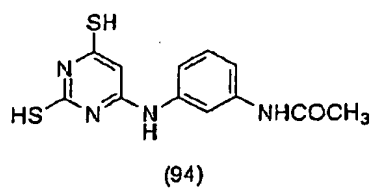
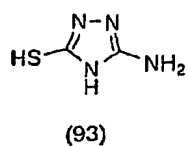
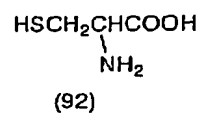
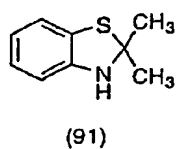
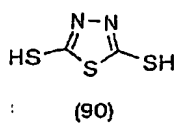
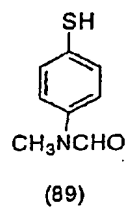
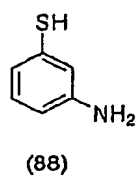
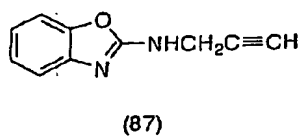
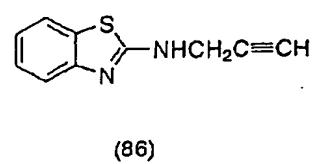
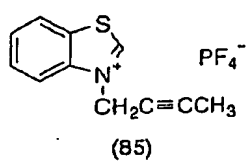
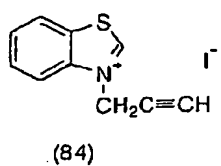
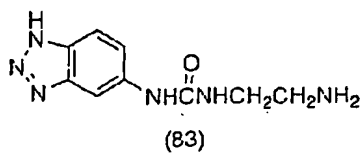
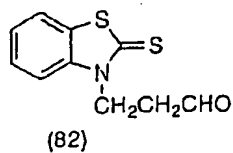
[0257]

[Formula 45]



[0258]

[Formula 46]



[0259]

Such compounds can each individually be synthesized in accordance with a known method.

The compounds represented by the formula (I) can be used either each individually or in combination of 2 or more types. When 2 or more types of compounds are used, they may be added in a same layer or in different layers. Methods of such addition may be different from one another.

[0260]

The compound represented by the compound (I) according to the invention is preferably added in a silver halide emulsion layer and more preferably added therein at the time of preparing the emulsion. When the compound is added at the time of preparing the emulsion, the compound can be added in any step of a preparation process; examples of such steps include a grain-forming step of a silver halide, a step before starting a desalting step, the desalting step, a step before starting a chemical ripening step, the chemical ripening step, and a step before preparing a final emulsion. The compound can be added in 2 or more steps in a multiple addition manner. Although the compound is preferably added in the emulsion layer, the compound is first added in not only the emulsion layer but also a protective layer or an intermediate layer adjacent to the emulsion layer and, then, allowed to be diffused at the time



of coating.

Although substantially depending on the above-described addition methods or a chemical species to be added, a quantity of the compound to be added is, based on 1 mol of the photosensitive silver halide, in the range of ordinarily from  $1 \times 10^{-6}$  mol to 1 mol, preferably from  $1 \times 10^{-5}$  mol to  $5 \times 10^{-1}$  mol, and more preferably from  $1 \times 10^{-4}$  mol to  $1 \times 10^{-1}$  mol.

[0261]

The compound represented by the formula (I) can be dissolved in water, a water-soluble solvent such as methanol or ethanol, or any mixtures thereof and, then, added. On this occasion, a pH of the resultant solution may be adjusted by an acid or a base, and, further, a surfactant may simultaneously be present in the solution. Still further, the compound can be dissolved in a high-boiling solvent to prepare an emulsify-dispersion and, then, the compound can be added in a form of the thus-prepared emulsify-dispersion. In another case, the compound can be added in a form of a solid dispersion.

[0262]

#### 11) Sensitizing Dye

As for sensitizing dyes applicable to the invention, a sensitizing dye capable of spectrally sensitizing the silver halide grain in a desired wavelength region when adsorbed on

the silver halide grain and having spectral sensitivity appropriate to spectral characteristics of an exposure light source can advantageously be selected. It is preferable that the photothermographic material according to the invention is spectrally sensitized such that it has a spectral sensitive peak, particularly, in a range from 600 nm to 900 nm, or in a range from 300 nm to 500 nm. The sensitizing dyes and addition methods thereof are described in paragraphs [0103] to [0109] of JP-A No. 11-65021, as compounds represented by the formula (II) in JP-A No. 10-186572, as dyes represented by the formula (I) in JP-A No. 11-119374, in paragraph [0106] of JP-A No. 11-119374, USP No. 5,510,236, as dyes mentioned in Example 5 in USP No. 3,871,887, in JP-A No. 2-96131, as dyes disclosed in JP-A No. 59-48753, in pp. 19 (line 38) to 20 (line 35) of EP-A No. 0803764A1, Japanese Patent Application Nos. 2000-86865, 2000-102560, and 2000-205399, and the like. These sensitizing dyes may be used either alone or in combination of 2 or more types.

[0263]

A quantity of the sensitizing dye according to the invention to be added is, though desirably varying depending on sensitivity or fogging performance, preferably in a range from  $10^{-6}$  mol to 1 mol, and more preferably from  $10^{-4}$  mol to  $10^{-1}$  mol, based on 1 mol of silver halide in an image-forming layer

in each case.

[0264]

According to the invention, in order to enhance spectral sensitizing efficiency, a super-sensitizer can be used. As for such super-sensitizers according to the invention, mentioned are compounds as described in, for example, EP-A No. 587,338, USP Nos. 3,877,943 and 4,873,184, JP-A Nos. 5-341432, 11-109547 and 10-111543.

[0265]

#### 12) Simultaneous Use of Silver Halides

In the photosensitive silver halide emulsion in the photothermographic material according to the invention, one type thereof may be used, or 2 or more types thereof (for example, those having different average grain sizes, different halogen compositions, different crystal habits or different chemical sensitization conditions from one another) may simultaneously be used. Using a plurality of types of photosensitive silver halides having different extents of sensitivity from one another allows gradation to be adjusted. Related technologies are described in, for example, JP-A Nos. 57-119341, 53-106125, 47-3929, 48-55730, 46-5187, 50-73627 and 57-150841. Sensitivity difference between any two emulsions is preferably 0.2 logE or more.

[0266]

13) Mixing of Silver Halide and Organic Silver Salt

It is particularly preferable that the photosensitive silver halide grain according to the invention is formed under a condition in which a non-photosensitive organic silver salt is not present and, then, chemically sensitized. Such procedure is taken because a method in which the silver halide is formed by adding a halogenating agent to the organic silver salt can not attain sufficient sensitivity in some cases.

As for methods for mixing the silver halide and the organic silver salt, mentioned is a method in which the photosensitive silver halide and the organic silver salt which have separately been prepared from one the other are mixed by, for example, a high-speed stirrer, a ball mill, a sand mill, a colloid mill, a vibration mill or a homogenizer, a method in which the photosensitive silver halide which has previously been prepared is mixed at an appropriate timing in the process of preparing the organic silver salt or the like to prepare the organic silver salt. Any of these methods can favorably obtain an effect according to the invention.

[0267]

14) Mixing of Silver Halide to Coating Solution

A preferable timing at which the silver halide according

to the invention is added to a coating solution for an image-forming layer may be during a period of from 180 minutes before coating is performed till immediately before the coating is performed, and preferably during a period of from 60 minutes before the coating is performed till 10 seconds before the coating is performed; however, a method and a condition of such addition is not particularly limited, so long as an effect according to the invention can sufficiently be exhibited. Specific mixing methods include, for example, a method of mixing in a tank such that an average dwelling time, as calculated from an adding flow rate and a supplying flow rate to a coater, is allowed to be within a predetermined duration, and a method of using a static mixer or the like as described, for example, in N. Harnby, M. F. Edwards & A. W. Nienow, (translated by Koji Takahashi), "*Liquid Mixing Technology*" Chap. 8, The Nikkan Kogyo Shimbun, Ltd. (1989).

[0268]

(Description of Organic Silver Salt)

The non-photosensitive organic silver salt which can be used in the invention is relatively stable to light, and is a silver salt which forms a silver image, when heated at 80°C or more in the presence of an exposed photosensitive silver halide and a reduction agent. The organic silver salt may be any type of an organic substance containing a source which can

reduce a silver ion. Such non-photosensitive organic silver salts are described in, for example, paragraphs [0048] and [0049] of JP-A No. 10-62899, pp. 18 (line 24) to 19 (line 37) of EP-A No. 0803764A1, EP-A No. 0962812A1, JP-A Nos. 11-349591, 2000-7683, and 2000-72711. Silver salts of organic acids, particularly, long chain aliphatic carboxylic acids (each having from 10 to 30 carbon atoms, preferably from 15 to 28 carbon atoms) are preferable. Preferable examples of such organic silver salts include silver behenate, silver arachidate, silver stearate, silver oleate, silver laurate, silver caproate, silver myristate, silver palmitate, and mixtures thereof. According to the invention, it is preferable to use an organic acid silver salt in which a silver behenate content is from 50 mol% to 100 mol% among these organic silver salts. It is particularly preferable that the silver behenate content is from 75 mol% to 98 mol%.

[0269]

A shape of the organic silver salt that can be used for the invention is not particularly limited, and any form of acicular, rod-like, tabular, and scaly forms is permissible.

However, according to the invention, the organic silver salt in the scaly form is preferable. The term "scaly organic silver salts" as used herein are defined as described below. An organic silver salt is observed under an electron microscope,

and a shape of an organic silver salt grain is approximated to a rectangular parallelepiped. Three different edges of the rectangular parallelepiped are represented as a, b and c in which a is the shortest, c is the longest (c and b may be same with each other). From the shorter edges a and b, x is obtained according to the following equation:

$$x=b/a$$

[0270]

Values of x are obtained for about 200 grains in a same manner as described above, and an average thereof x (average) is obtained. Samples that satisfy the relationship of x (average) $\geq 1.5$  are defined as being scaly. Scaly grains preferably satisfy  $30 \geq x$  (average) $\geq 1.5$ , more preferably  $15 \geq x$  (average) $\geq 1.5$ . In this connection, acicular grains satisfy  $1 \leq x$  (average) $< 1.5$ .

[0271]

In scaly grains, it is understood that a corresponds to thickness of tabular grains in which main planes are defined by the sides of b and c. An average of a is preferably from 0.01  $\mu\text{m}$  to 0.3  $\mu\text{m}$ , and more preferably from 0.1  $\mu\text{m}$  to 0.23  $\mu\text{m}$ . An average of c/b is preferably from 1 to 6, more preferably from 1 to 4, still more preferably from 1 to 3, and particularly preferably from 1 to 2.

[0272]

A grain size distribution of the organic silver salts is preferably monodispersed. The term "monodispersed" as used herein is intended to mean that the percentage of a value obtained by dividing the standard deviation of the length of the short axis or long axis by the length of the short axis or long axis, respectively, is preferably 100% or less, more preferably 80% or less, and still more preferably 50% or less. As for a method for measuring the shape of the organic silver salt, the shape of the organic silver salt can be determined by a method utilizing a transmission electron microscope image of an organic silver salt dispersion. Another method for determining the monodispesibility is a method involving obtaining the standard deviation of a volume weight average diameter of the organic silver salt. The percentage (coefficient of variation) of the value obtained by dividing the standard deviation by the volume weight average diameter is preferably 100% or less, more preferably 80% or less, and still more preferably 50% or less. As for a measurement method, for example, laser light is irradiated on the organic silver salt dispersed in the solution to allow the light to be scattered and, then, an autocorrelation function of fluctuation of the resultant scattered light against time is obtained to measure a grain size (volume weight average diameter) and, thereafter, the monodispesibility can be



obtained from the thus-measured grain size.

[0273]

A preparation method and a dispersion method of the organic acid silver according to the invention can adopt any one of known methods and the like. Methods described in, for example, JP-A No. 10-62899, EP-A Nos. 0803763A1, and 0962812A1, JP-A Nos. 11-349591, 2000-7683, 2000-72711, 2001-163827, 2001-163889, 2001-163890, and 11-203413, and Japanese Patent Application Nos. 2000-90093, 2000-195621, 2000-191226, 2000-213813, 2000-214155 and 2000-191226 can be of reference.

[0274]

According to the invention, it is possible to prepare a photosensitive material by mixing an aqueous dispersion of the organic silver salt and an aqueous dispersion of the photosensitive silver salt. When such mixing is performed, it is a favorable method for the purpose of appropriately adjusting photographic properties to mix two or more types of aqueous dispersions of organic silver salts and two or more types of aqueous dispersion of the photosensitive silver salt.

[0275]

Although the organic silver salt according to the invention can be used in a desired quantity, a silver quantity

is preferably in a range from 0.1 g/m<sup>2</sup> to 5 g/m<sup>2</sup>, more preferably from 1 g/m<sup>2</sup> to 3 g/m<sup>2</sup> and particularly preferably from 1.2 g/m<sup>2</sup> to 2.5 g/m<sup>2</sup>.

[0276]

(Description of Reduction Agent)

The photothermographic material according to the invention comprises a reduction agent for an organic silver salt. The reduction agent may be any substance (preferably organic substance) which can reduce a silver ion to metallic silver. Examples of such reduction agents include those as described in paragraphs [0043] to [0045] of JP-A No. 11-65021, and in pp. 7 (line 34) to 18 (line 12) of EP-A No. 0803764.

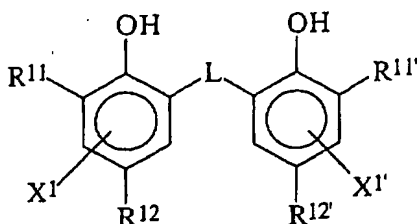
[0277]

A preferable reduction agent according to the invention is a so-called hindered phenolic reduction agent or bisphenolic reduction agent having a substituent in an ortho position of a phenolic hydroxyl group. Particularly, favorable are compounds represented by the following formula (R):

[0278]

Formula (R)

[Formula 47]



[0279]

wherein  $R^{11}$  and  $R^{11'}$  each independently represent an alkyl group having from 1 to 20 carbon atoms;

$R^{12}$  and  $R^{12'}$  each independently represent a hydrogen atom or a substituent which can be substituted in a benzene ring;

L represents a group of  $-S-$  or  $-CHR^{13}-$ , wherein  $R^{13}$  represents a hydrogen atom or an alkyl group having from 1 to 20 carbon atoms; and

$X^1$  and  $X^{1'}$  each independently represent a hydrogen atom or a group which can be substituted in a benzene ring.

[0280]

Now, each substituent will be described in detail.

1)  $R^{11}$  and  $R^{11'}$

$R^{11}$  and  $R^{11'}$  each independently represent an alkyl group, which is substituted or non-substituted, having from 1 to 20 carbon atoms. A substituent of the alkyl group is not particularly limited and preferable examples of such substituents include an aryl group, a hydroxyl group, an alkoxy group, an aryloxy group, an alkylthio group, an arylthio group, an acylamino group, a sulfonamide group, a sulfonyl group, a

phosphoryl group, an acyl group, a carbamoyl group, an ester group, and a halogen atom.

[0281]

2)  $R^{12}$  and  $R^{12'}$ , and  $X^1$  and  $X^{1'}$

$R^{12}$  and  $R^{12'}$  each independently represent a hydrogen atom or a group which can be substituted in a benzene ring.

$X^1$  and  $X^{1'}$  each independently represent a hydrogen atom or a group which can be substituted in a benzene ring. Preferable examples of such groups which can each be substituted in a benzene ring include an alkyl group, an aryl group, a halogen atom, an alkoxy group and an acylamino group.

[0282]

3) L

L represents a group of  $-S-$  or  $-CHR^{13}-$ , wherein  $R^{13}$  represents a hydrogen atom or an alkyl group having from 1 to 20 carbon atoms, in which the alkyl group may have a substituent.

Specific examples of such alkyl groups which are non-substituted  $R^{13}$  include a methyl group, an ethyl group, a propyl group, a butyl group, a heptyl group, an undecyl group, an isopropyl group, a 1-ethylpentyl group, and a 2,4,4-trimethylpentyl group.

[0283]

Examples of substituents of the alkyl groups, being same as those of  $R^{11}$ , include a halogen atom, an alkoxy group, an alkylthio group, an aryloxy group, an arylthio group, an acylamino group, a sulfonamide group, a sulfonyl group, a phosphoryl group, an oxycarbonyl group, a carbamoyl group, and a sulfamoyl group.

[0284]

#### 4) Preferred Substituent

$R^{11}$  and  $R^{11'}$  are preferably a secondary or tertiary alkyl group having from 3 to 15 carbon atoms; examples of such alkyl groups include an isopropyl group, an isobutyl group, a t-butyl group, a t-amyl group, a t-octyl group, a cyclohexyl group, a cyclopentyl group, a 1-methylcyclohexyl group, and a 1-methylcyclopropyl group.  $R^{11}$  and  $R^{11'}$  are more preferably a tertiary alkyl group having from 4 to 12 carbon atoms, still more preferably a t-butyl group, a t-amyl group, and a 1-methylcyclohexyl group, and most preferably a t-butyl group.

[0285]

$R^{12}$  and  $R^{12'}$  are each independently preferably an alkyl group having from 1 to 20 carbon atoms; and specific examples of such alkyl groups include a methyl group, an ethyl group, a propyl group, a butyl group, an isopropyl group, a t-butyl group, a t-amyl group, a cyclohexyl group, a 1-methylcyclohexyl

group, a benzyl group, a methoxymethyl group, and a methoxyethyl group, and more preferably a methyl group, an ethyl group, a propyl group, an isopropyl group and a t-butyl group.

[0286]

$X^1$  and  $X^{1'}$  are each preferably a hydrogen atom, a halogen atom, and an alkyl group, and more preferably a hydrogen atom.

[0287]

L is preferably a  $-\text{CHR}^{13}-$  group.

[0288]

$R^{13}$  is preferably a hydrogen atom or an alkyl group having from 1 to 15 carbon atoms, and preferable examples of such alkyl groups include a methyl group, an ethyl group, a propyl group, an isopropyl group, and a 2,4,4-trimethylpentyl group. Particularly preferable examples of  $R^{13}$  include a hydrogen atom, a methyl group, a propyl group, and an isopropyl group.

[0289]

When  $R^{13}$  is a hydrogen atom,  $R^{12}$  and  $R^{12'}$  are each preferably an alkyl group having from 2 to 5 carbon atoms in which an ethyl group and a propyl group are more preferable and an ethyl group is most preferable.

[0290]

When  $R^{13}$  is a primary or secondary alkyl group having from 1 to 8 carbon atoms,  $R^{12}$  and  $R^{12'}$  are each preferably a methyl group. As for the primary or secondary alkyl group each having from 1 to 8 carbon atoms of  $R^{13}$ , a methyl group, an ethyl group, a propyl group, an isopropyl group are more preferable, and a methyl group, an ethyl group and a propyl group are still more preferable.

[0291]

When  $R^{11}$ ,  $R^{11'}$ ,  $R^{12}$ , and  $R^{12'}$  are each a methyl group,  $R^{13}$  is preferably a secondary alkyl group. On this occasion, as for such secondary alkyl groups of  $R^{13}$ , an isopropyl group, an isobutyl group, and a 1-ethylpentyl group are preferable, and an isopropyl group is more preferable.

[0292]

Various types of thermal developing properties of these reduction agents can be changed by combining  $R^{11}$ ,  $R^{11'}$ ,  $R^{12}$ ,  $R^{12'}$ , and  $R^{13}$ . Since the thermal developing properties of reduction agents can be adjusted by simultaneously using at least two types of reduction agents at various types of combining ratios, it is preferable, though depending on applications, to use at least two types of reduction agents in combination.

[0293]

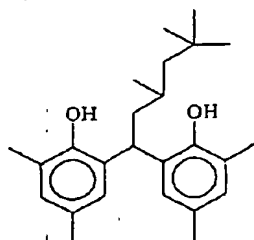
Specific examples of compounds represented by the formula (R) according to the invention are described below; however, the invention is by no means limited thereto.



[0294]

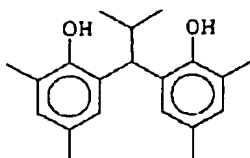
[Formula 48]

( R - 1 )



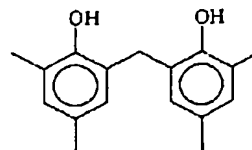
( R - 4 )

( R - 2 )

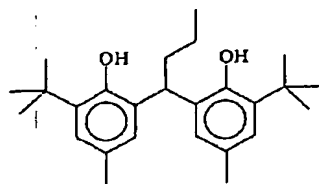


( R - 5 )

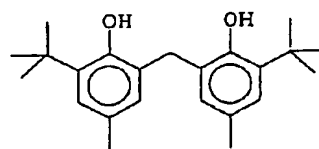
( R - 3 )



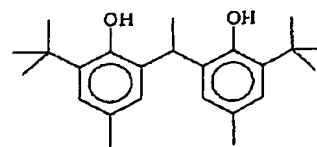
( R - 6 )



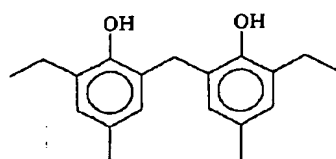
( R - 7 )



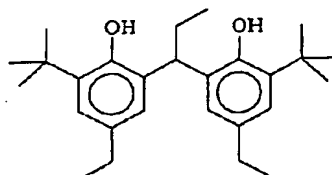
( R - 8 )



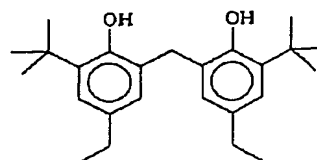
( R - 9 )



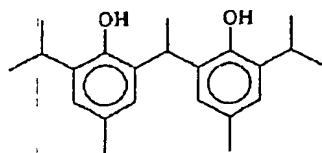
( R - 1 0 )



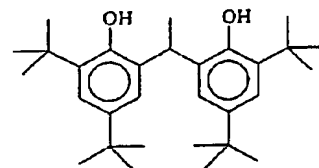
( R - 1 1 )



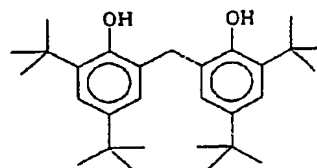
( R - 1 2 )



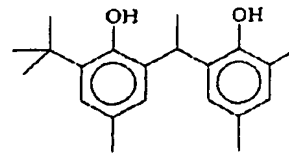
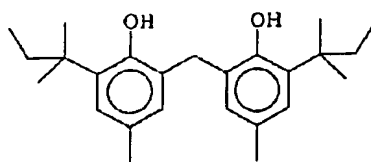
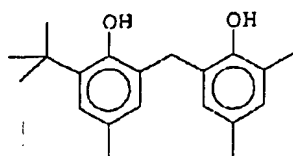
( R - 1 3 )



( R - 1 4 )



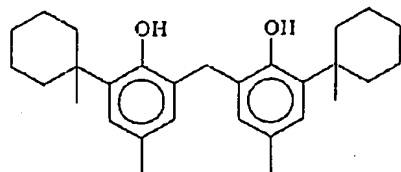
( R - 1 5 )



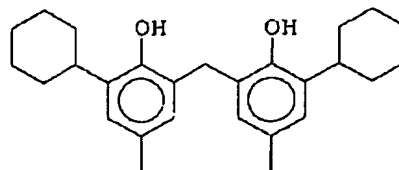
[0295]

[Formula 49]

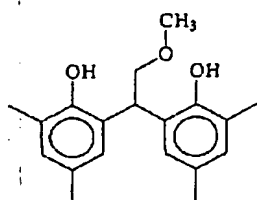
(R-16)



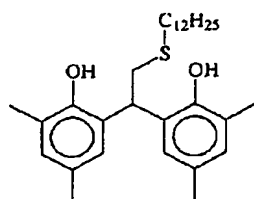
(R-17)



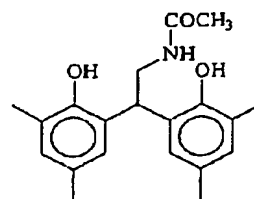
(R-18)



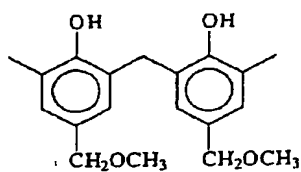
(R-19)



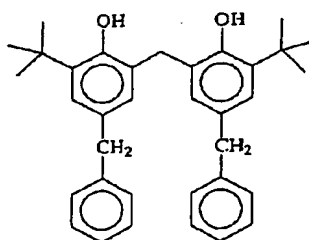
(R-20)



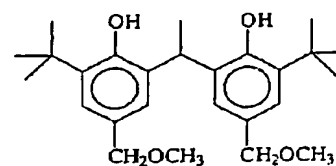
(R-21)



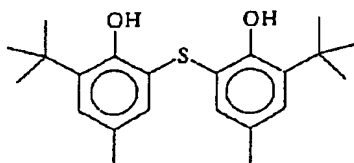
(R-22)



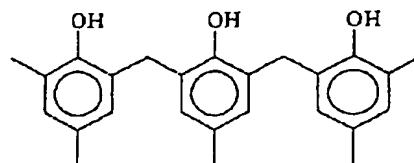
(R-23)



(R-24)



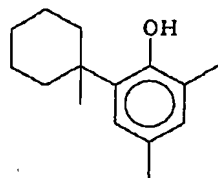
(R-25)



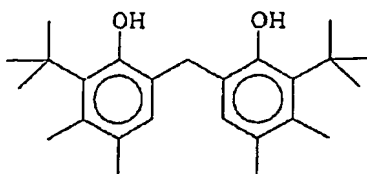
[0296]

[Formula 50]

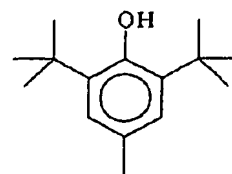
(R - 26)



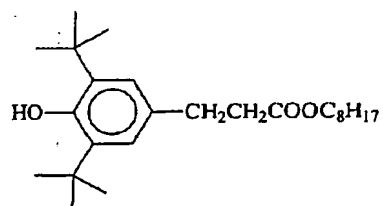
(R - 27)



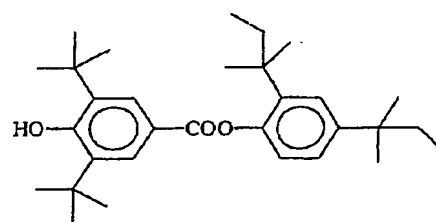
(R - 28)



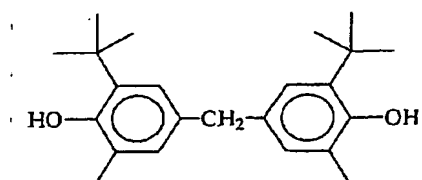
(R - 29)



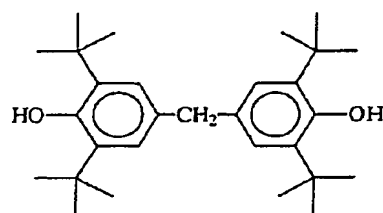
(R - 30)



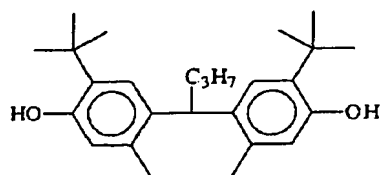
(R - 31)



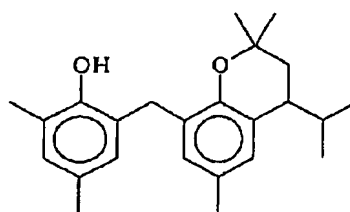
(R - 32)



(R - 33)



(R - 34)



[0297]

Particularly, compounds of from (R-1) to (R-20) are preferable.

[0298]

A quantity of the reduction agent to be added according to the invention is preferably in a range from 0.01 g/m<sup>2</sup> to 5.0 g/m<sup>2</sup>, more preferably from 0.1 g/m<sup>2</sup> to 3.0 g/m<sup>2</sup> and, based on 1 mol of silver on a surface having an image-forming layer, preferably in a range from 5 mol% to 50 mol% and more preferably from 10 mol% to 40 mol%.

[0299]

Although the reduction agent according to the invention can be added in the image-forming layer comprising the organic silver salt and the photosensitive silver halide, and a layer adjacent thereto, it is more preferable to allow the reduction agent to be contained in the image-forming layer.

[0300]

The reduction agent according to the invention may be contained in the coating solution in any form of solution form, emulsify-dispersion form, solid fine grain dispersion form and the like and the resultant coating solution may be contained in the photosensitive material.

[0301]

As for well known emulsify-emulsion methods, mentioned is a method in which the reduction agent is dissolved by using an auxiliary solvent such as dibutyl phthalate, tricresyl phosphate, glyceryl triacetate, an oil such as diethyl phthalate, ethyl acetate, and cyclohexanone and, then, the resultant solution was mechanically treated to prepare an emulsion.

[0302]

Further, as for solid fine grain dispersion methods, mentioned is a method in which the reduction agent is dispersed in an appropriate solvent such as water by using a ball mill, a colloid mill, a vibration ball mill, a sand mill, a jet mill, a roller mill or an ultrasonic wave to prepare a solid dispersion. Preferably, the dispersion method is that of using the sand mill. On this occasion, any one of a protective colloid (for example, polyvinyl alcohol), and a surfactant (for example, an anionic surfactant such as sodium triisopropyl naphthalene sulfonate that is a mixture of different types of such sulfonates in which substitution positions of three isopropyl groups are different from one another) may be used. An antiseptic agent (for example, a sodium salt of benzisothiazolinone) is allowed to be contained in an aqueous dispersion.

[0303]

A particularly favorable method is the solid fine grain dispersion method. The reduction agent is added as fine grains having an average grain size in a range from 0.01  $\mu\text{m}$  to 10  $\mu\text{m}$ , preferably from 0.05  $\mu\text{m}$  to 5  $\mu\text{m}$ , and more preferably from 0.1  $\mu\text{m}$  to 1  $\mu\text{m}$ . According to the invention, it is preferable that any one of other solid dispersions is dispersed in the above-described ranges of grain sizes and, then, used.

[0304]

(Description of Development Accelerator)

In the photothermographic material according to the invention, sulfonamide phenolic compounds represented by the formula (A) as described in JP-A Nos. 2000-267222 and 2000-330234, hindered phenolic compounds represented by the formula (II) as described in JP-A No. 2001-92075, hydrazine-type compounds as described in JP-A No. 10-62895, and represented by the formula (I) as described in JP-A No. 11-15116, the formula (I) as described in JP-A No. 11-15116, or the formula (1) as described in Japanese Patent Application No. 2001-074278, and phenolic or naphthol-type compounds represented by the formula (2) as described in Japanese Patent Application No. 2000-76240 are favorably used. These development accelerators are used, against the reduction agent, in a range from 0.1 mol% to 20 mol%, preferably from 0.5 mol% to 10 mol%, and more preferably

from 1 mol% to 5 mol%. A method of introducing the development accelerator to the photosensitive material may be performed in a same manner as in the reduction agent and, particularly, it is preferably incorporated after being changed into a solid dispersion or an emulsify-dispersion. When the development accelerator is added as an emulsify-dispersion, it is preferable to add the development accelerator in a form of the emulsify-dispersion which has been prepared by emulsifying the development accelerator by simultaneously using a high-boiling solvent that is solid at room temperature and a low-boiling auxiliary solvent or in a form of a so-called oil-less emulsify-dispersion in which a high-boiling solvent is not used.

[0305]

Among the above-mentioned development accelerators, hydrazine compounds represented by the formula (1) in Japanese Patent Application No. 2001-074278 and phenol or naphthol compounds represented by the formula (2) in Japanese Patent Application No. 2000-76240 are more preferred in the invention.

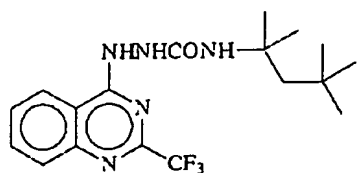
[0306]

Specific examples of development accelerators according to the invention are described below; however, the invention is by no means limited thereto.

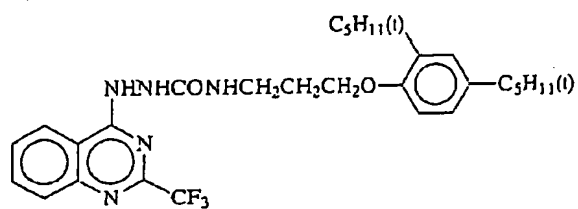
[0307]

[Formula 51]

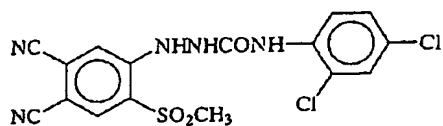
(A-1)



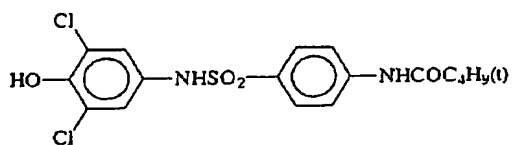
(A-2)



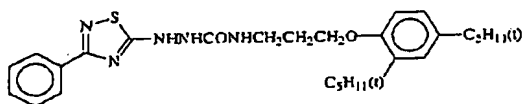
(A-3)



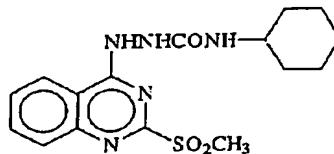
(A-4)



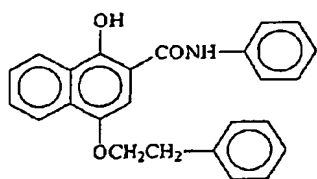
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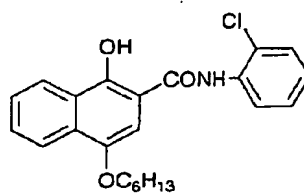
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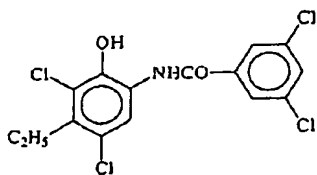
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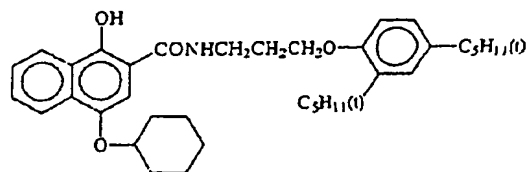
(A-8)



(A-9)



(A-10)





[0308]

(Description of Hydrogen Bonding-Type Compound)

When a reduction agent according to the invention has an aromatic hydroxyl group (-OH), or an amino group, it is preferable that a non-reducible compound having a group capable of forming a hydrogen bond with an amino group can simultaneously be used.

[0309]

Examples of groups each capable of forming a hydrogen bond include a phosphoryl group, a sulfoxide group, a sulfonyl group, a carbonyl group, an amide group, an ester group, a urethane group, a ureido group, a t-amino group, and a nitrogen-containing aromatic group. Among these groups, compounds each having a phosphoryl group, a sulfoxide group, an amide group (however, having no >N-H group; being blocked in form of >N-Ra, in which Ra represents a substituent exclusive of H), a urethane group (however, having no >N-H group; being blocked in form of >N-Ra, in which Ra represents a substituent exclusive of H), a ureido group (however, having no >N-H group; being blocked in form of >N-Ra, in which Ra represents a substituent exclusive of H) are preferable.

[0310]

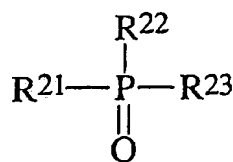
Particularly favorable hydrogen bonding-type compounds

according to the invention are compounds represented by the following formula (D):

[0311]

Formula (D)

[Formula 52]



[0312]

In the formula (D),  $\text{R}^{21}$ ,  $\text{R}^{22}$ , and  $\text{R}^{23}$  each independently represent an alkyl group, an aryl group, an alkoxy group, an aryloxy group, an amino group, or a heterocyclic group. These groups may be non-substituted or have a substituent.

[0313]

When any one of  $\text{R}^{21}$ ,  $\text{R}^{22}$ , and  $\text{R}^{23}$  has a substituent, examples of such substituents include a halogen atom, an alkyl group, an aryl group, an alkoxy group, an amino group, an acyl group, an acylamino group, an alkylthio group, an arylthio group, a sulfonamide group, an acyloxy group, an oxycarbonyl group, a carbamoyl group, a sulfamoyl group, a sulfonyl group and a phosphoryl group; on this occasion, the substituent is preferably an alkyl group or an aryl group; examples of such

alkyl groups and aryl groups include a methyl group, an ethyl group, an isopropyl group, a t-butyl group, a t-octyl group, a phenyl group, a 4-alkoxyphenyl group, and a 4-acyloxyphenyl group.

[0314]

Specific examples of such alkyl groups represented each independently by  $R^{21}$ ,  $R^{22}$ , and  $R^{23}$  include a methyl group, an ethyl group, a butyl group, an octyl group, a dodecyl group, an isopropyl group, a t-butyl group, a t-amyl group, a t-octyl group, a cyclohexyl group, a 1-methyl cyclohexyl group, a benzyl group, a phenethyl group, and a 2-phenoxypropyl group.

[0315]

Specific examples of such aryl groups include a phenyl group, a cresyl group, a xylyl group, a naphthyl group, a 4-t-butylphenyl group, a 4-t-octylphenyl group, a 4-anisidyl group, and a 3,5-dichlorophenyl group.

[0316]

Specific examples of such alkoxy groups include a methoxy group, an ethoxy group, a butoxy group, an octyloxy group, a 2-ethylhexyloxy group, a 3,5,5-trimethyl hexyloxy group, a dodecyloxy group, a cyclohexyloxy group, a 4-methyl cyclohexyloxy group, and a benzyloxy group.

[0317]

Specific examples of such aryloxy groups include a phenoxy group, a cresyloxy group, an isopropylphenoxy group, a 4-t-butylphenoxy group, a naphthoxy group, and a biphenyloxy group.

[0318]

Specific examples of such amino groups include a dimethylamino group, a diethylamino group, a dibutylamino group, a dioctylamino group, an N-methyl-N-hexylamino group, a dicyclohexylamino group, a diphenylamino group, and an N-methyl-N-phenylamino group.

[0319]

As for  $R^{21}$ ,  $R^{22}$ , and  $R^{23}$ , an alkyl group, an aryl group, an alkoxy group, and aryloxy group are preferable. From the standpoint of an effect according to the invention, it is preferable that at least one of  $R^{21}$ ,  $R^{22}$  and  $R^{23}$  is an alkyl group or an aryl group, and it is more preferable that at least two of  $R^{21}$ ,  $R^{22}$  and  $R^{23}$  are an alkyl group or an aryl group. Further, taking availability at a low price into consideration, it is preferable that  $R^{21}$ ,  $R^{22}$ , and  $R^{23}$  are a same group with one another.

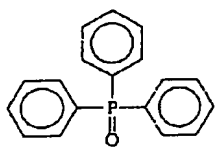
[0320]

Specific examples of hydrogen bonding-type compounds are described below, starting with compounds represented by the formula (D) according to the invention; however, the invention is by no means limited thereto.

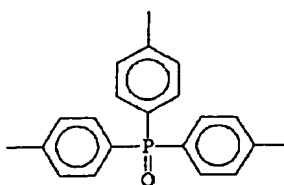
[0321]

[Formula 53]

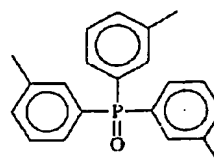
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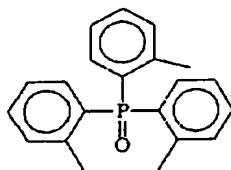
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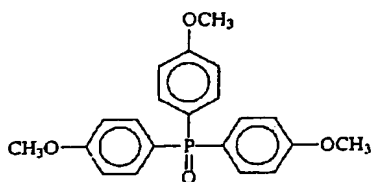
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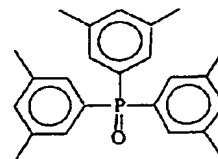
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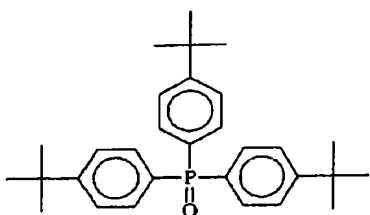
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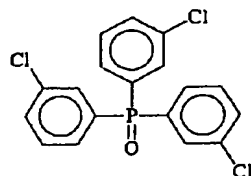
(D-6)



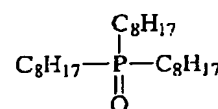
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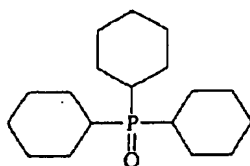
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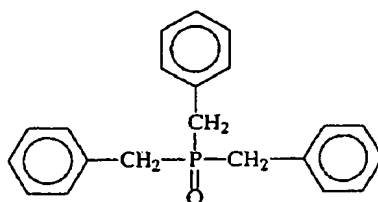
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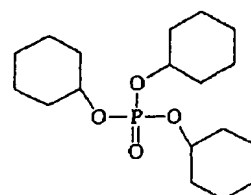
(D-10)



(D-11)



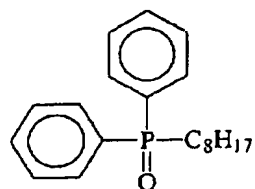
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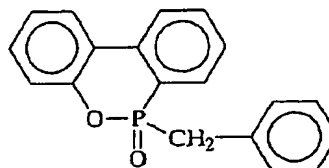
[0322]

[Formula 54]

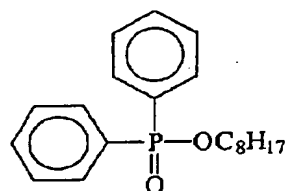
(D-13)



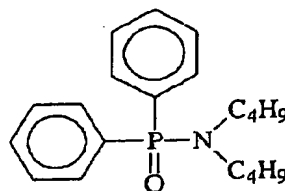
(D-14)



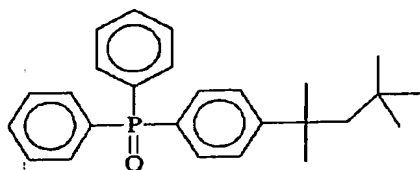
(D-15)



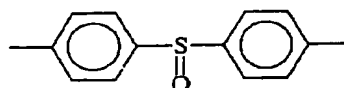
(D-16)



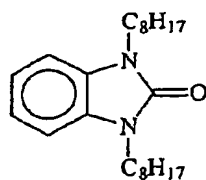
(D-17)



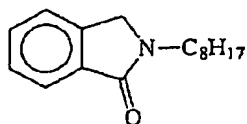
(D-18)



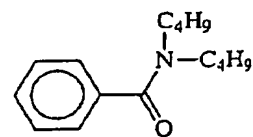
(D-19)



(D-20)



(D-21)



[0323]

Specific examples of the hydrogen bonding-type compounds further include those as described in Japanese Patent Application Nos. 2000-192191 and 2000-194811.

[0324]

The hydrogen bonding-type compound according to the invention can be contained in the coating solution, in a same manner as in the reduction agent, in a form of the solution form, the emulsify-dispersion form, or the solid fine grain dispersion form and, then, the resultant coating solution can be contained in the photosensitive material. The hydrogen bonding-type compound according to the invention forms a complex in a solution state by forming a hydrogen bond with a compound having a phenolic hydroxyl group. The complex, though depending on combinations of the reduction agents and the compounds represented by the formula (A) according to the invention, can be isolated in a crystal state.

[0325]

It is particularly favorable from the standpoint of obtaining a consistent performance that the thus-isolated crystal powders are used as the solid fine grain dispersion. Further, favorably used is a method in which the reduction agent and the hydrogen bonding-type compound according to the

invention are mixed in respective powder states with each other and, then, dispersed by using an appropriate dispersing agent by utilizing a sand-grinder mill or the like to form a complex at the time of such dispersion.

[0326]

The hydrogen bonding-type compound according to the invention is used, against the reduction agent, preferably in a range from 1 mol% to 200 mol%, more preferably from 10 mol% to 150 mol% and still more preferably from 30 mol% to 100 mol%.

[0327]

(Description of Binder)

A binder in an organic silver salt-containing layer according to the invention may be any type of polymers. Such binders are preferably transparent or semi-transparent and ordinarily colorless; examples of the binders include natural resins or polymers and copolymers, synthetic resins or polymers and copolymers, and other media which form a film; and specific examples thereof include gelatins, rubbers, poly(vinyl alcohol)s, hydroxyethyl celluloses, cellulose acetates, cellulose acetate butyrates, poly(vinylpyrrolidone)s, casein, starch, poly(acrylic acid)s, poly(methylmethacrylic acid)s, poly(vinyl chloride)s, poly(methacrylic acid)s, styrene/maleic acid anhydride copolymers,



styrene/acrylonitrile copolymers, styrene/butadiene copolymers, poly(vinyl acetal)s (for example, poly(vinyl formal) and poly(vinyl butylal)), poly(ester)s, poly(urethane)s, phenoxy resins, poly(vinylidene chloride)s, poly(epoxide)s, poly(carbonate)s, poly(vinyl acetate)s, poly(olefin)s, cellulose esters and poly(amide)s. The binders may be provided in water or an organic solvent or as an emulsion for film forming.

[0328]

According to the invention, a glass transition temperature (hereinafter referred to also as "Tg") of the binder in the organic silver salt-containing layer is preferably in a range from 10°C to 80°C, more preferably from 20°C to 70°C, and still more preferably from 23°C to 65°C.

[0329]

Further, according to the invention, the Tg is calculated with the following equation:

$$1/T_g = \sum (X_i/T_{gi})$$

[0330]

In this case, it is assumed that the polymer is formed by copolymerization of n monomer components from i=1 to i=n. X<sub>i</sub> is a weight ratio ( $\sum X_i = 1$ ) of the i-th monomer and T<sub>gi</sub> is

a glass transition temperature (at an absolute temperature) of a homopolymer of the  $i$ -th monomer, provided that  $\sum$  is a sum of from  $i=1$  to  $i=n$ .

Further, for the value ( $T_{gi}$ ) of glass transition temperature of the homopolymer made from each monomer, values described in J. Brandrup and E. H. Immergut, *Polymer Handbook*, 3rd Edition, Willey-Interscience (1989) have been adopted.

[0331]

These polymers which become binders may be used as a single type or in combination of two or more types according to necessity. A combination of a polymer having  $T_g$  of 20°C or more and a polymer having  $T_g$  of less than 20°C may also be used. When two or more types of polymers having different  $T_g$  values from one another are used in blending, it is preferable that a weight average  $T_g$  resides in the ranges described above.

[0332]

According to the invention, properties of the photothermographic material are improved when the organic silver salt-containing layer has been formed by first applying a coating solution comprising 30% by mass or more of water of the total solvent and, then, drying and, further, when the binder in the organic silver salt-containing layer is soluble or dispersible in an aqueous solvent (a water solvent), and,

particularly, when the binder comprises a latex of polymer in which an equilibrium moisture content at 25°C 60% RH is 2% by mass or less.

The most preferred form is such a form as is prepared such that an ionic conductivity becomes 2.5 mS/cm or less. As for such preparation method, mentioned is a purification method using a functional membrane for separation after a polymer is synthesized.

[0333]

The aqueous solvent mentioned here in which the polymer is soluble or dispersible means water or a mixture of water and a water-miscible organic solvent in a quantity of 70% by mass or less.

Examples of such water-miscible organic solvents include alcohol solvents such as methyl alcohol, ethyl alcohol and propyl alcohol; cellosolve solvents such as methyl cellosolve, ethyl cellosolve and butyl cellosolve; ethyl acetate; and dimethyl formamide.

[0334]

Further, the term "equilibrium moisture content at 25°C 60% RH" as used herein can be expressed by using a weight  $W_1$  of a polymer in an equilibrium with moisture conditioning under the atmosphere at 25°C 60% RH and a weight  $W_0$  of the polymer

in the absolutely dry state, as shown in the following equation:

The equilibrium moisture content at 25°C 60%

$$RH = \{(W1 - W0) / W0\} \times 100 \text{ (\% by mass)}$$

Regarding a definition and a measurement method of the moisture content, for example, *Testing Methods of Polymer Materials, Polymer Engineering Course 14*, compiled by the Society of Polymer Science of Japan, Chijin Shokan Co., Ltd. can be referred.

[0335]

An equilibrium moisture content of the binder polymer according to the invention at 25°C 60% RH is preferably 2% by mass or less, more preferably in a range from 0.01% by mass to 1.5% by mass, and still more preferably from 0.02% by mass to 1% by mass.

[0336]

As for the binders according to the invention, a polymer dispersible in an aqueous solvent is particularly preferred. Examples of dispersed states include a latex in which fine grains of a water-insoluble and hydrophobic polymer are dispersed and a dispersion in which polymer molecules are dispersed in a molecular state or a micelle-forming state. Both of them are favorable. An average grain diameter of dispersed grains is preferably in a range from 1 nm to 50,000 nm, and more preferably

from approximately 5 nm to approximately 1,000 nm. A grain diameter distribution of the dispersed grains is not particularly limited and either of dispersed grains having a broad grain diameter distribution or having a monodispersed grain diameter distribution may be used.

[0337]

According to the invention, examples of preferably usable embodiments of polymers dispersible in aqueous solvents include hydrophobic polymers such as acrylic polymers, poly(ester)s, rubbers (for example, SBR resins), poly(urethane)s, poly(vinyl chloride)s, poly(vinyl acetate)s, poly(vinylidene chloride)s and poly(olefin)s. These polymers may be a straight-chain polymer, a branched-chain polymer, a cross-linked polymer, a so-called homopolymer in which monomers of a single type have been polymerized, or a copolymer in which monomers of two or more types have been polymerized. In case of the copolymer, it may be either of a random copolymer or a block copolymer.

[0338]

A molecular weight of these polymers is, in terms of the number average molecular weight, in a range from 5,000 to 1,000,000 and preferably from 10,000 to 200,000. When a polymer having an unduly small molecular weight is used, dynamic strength of the emulsion layer becomes insufficient. When a polymer

having an unduly large molecular weight is used, film-forming properties are deteriorated. None of these cases is preferable.

[0339]

Specific examples of preferable polymer latices include materials described below. These materials are each expressed in terms of a starting monomer; a value in each parenthesis is indicated in terms of "% by mass"; and a molecular weight means a number average molecular weight. In a case in which a multi-functional monomer is used, the concept of molecular weight can not be applied, since a cross-linked structure is formed. Accordingly, such a case is marked as "cross-linking" to omit description of molecular weight. Tg denotes a glass transition temperature.

[0340]

P-1; a latex (MW: 37,000; Tg: 61°C) of  
MMA(70)/EA(27)/MAA(3)

P-2; a latex (MW: 40,000; Tg: 59°C) of  
MMA(70)/2EHA(20)/St(5)/AA(5)

P-3; a latex (cross-linking; Tg: -17°C) of  
St(50)/Bu(47)/MAA(3)

P-4; a latex (cross-linking; Tg: 17°C) of  
St(68)/Bu(29)/AA(3)

P-5; a latex (cross-linking; Tg: 24°C) of

St(71)/Bu(26)/AA(3)

P-6; a latex (cross-linking ) of St(70)/ Bu(27)/IA(3)

P-7; a latex (cross-linking; Tg: 29°C) of  
St(75)/Bu(24)/AA(1)

P-8; a latex (cross-linking) of  
St(60)/Bu(35)/DVB(3)/MAA(2)

P-9; a latex (cross-linking) of  
St(70)/Bu(25)/DVB(2)/AA(3)

P-10; a latex (MW: 80,000) of  
VC(50)/MMA(20)/EA(20)/AN(5)/AA(5)

P-11; a latex (MW: 67,000) of VDC(85)/MMA(5)/EA(5)/MAA(5)

P-12; a latex (MW: 12,000) of Et(90)/MAA(10)

P-13; a latex (MW: 130,000; Tg: 43°C) of  
St(70)/2EHA(27)/AA(3)

P-14; a latex (MW 33,000; Tg: 47°C) of  
MMA(63)/EA(35)/AA(2)

P-15; a latex (cross-linking; Tg: 23°C) of  
St(70.5)/Bu(26.5)/AA(3)

P-16; a latex (cross-linking; Tg: 20.5°C) of  
St(69.5)/Bu(27.5)/AA(3)

[0341]

Abbreviations in the above structures denote respective  
monomers as follows:

MMA: methyl metacrylate; EA: ethy acrylate; MAA

methacrylic acid; 2EHA: 2-ethylhexyl acrylate; St: Styrene; Bu: Butadiene; AA: acrylic acid; DVB: divinyl benzene; VC: vinyl chloride; AN: acrylonitrile; VDC: vinylidene chloride; Et: ethylene; and IA: itaconic acid.

[0342]

Polymer latices described above are commercially available and such products as described below can be utilized. Examples of acrylic polymers include Cevian A-4635, 4718 and 4601 (manufactured by Daicel Chemical Industries, Ltd.) and Nipol Lx811, 814, 821, 820 and 857 (manufactured by Zeon Corp.). Examples of poly(ester)s include FINETEX ES650, 611, 675 and 850 (manufactured by Dainippon Ink & Chemicals Inc.) and WD-size and WMS (manufactured by Eastman Chemical Company). Examples of poly (urethane)s include HYDRAN AP10, 20, 30 and 40 (manufactured by Dainippon Ink & Chemicals Inc.). Examples of rubbers include LACSTAR 7310K, 3307B, 4700H and 7132C (manufactured by Dainippon Ink & Chemicals Inc.) and Nipol Lx416, 410, 438C and 2507 (manufactured by Zeon Corp.). Examples of poly(vinyl chloride)s include G351 and G576 (manufactured by Zeon Corp.). Examples of poly(vinylidene chloride)s include L502 and L513 (manufactured by Asahi Chemical Industry Co., Ltd.). Examples of poly (olefin)s include Chemipearl S120 and SA100 (manufactured by Mitsui Petrochemical Industries, Ltd.).

These polymer latices may be used as a single type or



as a blend of two or more types according to necessity.

[0343]

As for the polymer latices according to the invention, a latex of a styrene/butadiene copolymer, particularly, is preferred. It is preferable that a weight ratio of styrene monomer units to butadiene monomer units is in a range from 40:60 to 95:5. Further, it is preferable that a ratio of styrene monomer units together with butadiene monomer units in the copolymer is in a range from 60% by mass to 99% by mass. The range of preferable molecular weight is same as that described above.

[0344]

As for preferable latices of styrene/butadiene copolymers according to the invention, mentioned are P-3 to P-8, P-15 and P-16 as described above, LACSTAR-3307B, and 7132C, and Nipol Lx416 (all trade names) which are commercially available.

[0345]

To the organic silver salt-containing layer of the photosensitive material according to the invention, hydrophilic polymers such as gelatin, polyvinyl alcohol, methyl cellulose, hydroxypropyl cellulose and carboxymethyl cellulose may be added according to necessity.

[0346]

A quantity of each of these hydrophilic polymers to be added is, based on an entire binder quantity in the organic silver salt-containing layer, preferably 30% by mass or less, and more preferably 20% by mass or less.

[0347]

It is preferable that the organic silver salt-containing layer (namely, image-forming layer) according to the invention is formed by using a polymer latex as a binder. A quantity of the binder in the organic silver salt-containing layer is, in terms of a weight ratio of the entire binder/organic silver salt, preferably in a range from 1/10 to 10/1, and more preferably from 1/5 to 4/1.

[0348]

Further, the organic silver salt-containing layer like this ordinarily acts as a photosensitive layer (image-forming layer or emulsion layer) in which a photosensitive silver halide is contained as a photosensitive silver salt. A weight ratio of an entire binder/silver halide in such a case as described above is preferably in a range from 400 to 5, and more preferably from 200 to 10.

[0349]

The entire binder quantity in the image-forming layer according to the invention is preferably in a range from 0.2 g/m<sup>2</sup> to 30 g/m<sup>2</sup>, and more preferably from 1 g/m<sup>2</sup> to 15 g/m<sup>2</sup>. To the image-forming layer according to the invention, a cross-linking agent for executing cross-linking, a surfactant for improving coating properties and the like may be added.

[0350]

According to the invention, a solvent (for the purpose of simplicity, a solvent and a dispersing medium are unanimously expressed as solvents) of a coating solution for an organic silver salt-containing layer of the photosensitive material is preferably an aqueous solvent containing 30% by mass or more of water. As for components other than water, any types of water-miscible organic solvents such as methyl alcohol, ethyl alcohol, isopropyl alcohol, Methyl Cellosolve, Ethyl Cellosolve, dimethyl formamide, and ethyl acetate may be used. A water content of such solvent is more preferably 50% by mass or more, and still more preferably 70% by mass or more.

[0351]

Examples of preferable solvent compositions include, not only water=100, but also water/methyl alcohol=90/10, water/methyl alcohol=70/30, water/methyl alcohol/dimethyl

formamide=80/15/5, and water/methyl alcohol/ethyl cellosolve  
=85/10/5 and water/methyl alcohol/isopropyl alcohol=85/10/5  
(numerical values being indicated in terms of "% by mass").

[0352]

(Description of Antifoggant)

According to the invention, it is preferable to contain  
as an antifoggant any one of compounds which are represented  
by the following formula (H):

[0353]

Formula (H)             $Q - (Y)_n - C(Z_1) - (Z_2)X$

[0354]

wherein, Q represents an alkyl group, an aryl group or  
a heterocyclic group;

Y represents a divalent linking group;

n represents 0 or 1;

Z<sub>1</sub> and Z<sub>2</sub> each independently represent a halogen atom;

and

X represents a hydrogen atom or an electron-attracting  
group.

[0355]

Q preferably represents a phenyl group substituted by

an electron-attracting group in which the Hammett's substituent constant  $\sigma_p$  has a positive value. Regarding the Hammett's substituent constant, *Journal of Medicinal Chemistry*, Vol. 16, No. 11, pp. 1207-1216 (1973) can be referred.

[0356]

Examples of such electron-attracting groups include a halogen atom (for example, a fluorine atom ( $\sigma_p$  value: 0.06)), a chlorine atom ( $\sigma_p$  value: 0.23), a bromine atom ( $\sigma_p$  value: 0.23) or an iodine atom ( $\sigma_p$  value: 0.18)), a trihalomethyl group (for example, a tribromomethyl group ( $\sigma_p$  value: 0.29), a trichloromethyl group ( $\sigma_p$  value: 0.33) or a trifluoromethyl group ( $\sigma_p$  value: 0.54)), a cyano group ( $\sigma_p$  value: 0.66), a nitro group ( $\sigma_p$  value: 0.78), an aliphatic, aryl or a heterocyclic sulfonyl group (for example, a methane sulfonyl group ( $\sigma_p$  value: 0.72)), an aliphatic, aryl or a heterocyclic acyl group (for example, an acetyl group ( $\sigma_p$  value: 0.50) or a benzoyl group ( $\sigma_p$  value: 0.43)), an alkynyl group (for example, a group of  $C\equiv CH$  ( $\sigma_p$  value: 0.23)), an aliphatic, aryl or a heterocyclic oxycarbonyl group (for example, a methoxycarbonyl group ( $\sigma_p$  value: 0.45) and a phenoxycarbonyl group ( $\sigma_p$  value: 0.44)), a carbamoyl group ( $\sigma_p$  value: 0.36), a sulfamoyl group ( $\sigma_p$  value: 0.57), a sulfoxide group, a heterocyclic group and a phosphoryl group.

A  $\sigma_p$  value is preferably in a range from 0.2 to 2.0, and

more preferably from 0.4 to 1.0.

[0357]

Preferable electron-attracting groups are a carbamoyl group, an alkoxycarbonyl group, an alkylsulfonyl group, an alkylphosphoryl group, a carboxyl group, an alkyl- or aryl-carbonyl group, and an arylsulfonyl group; particularly preferable groups are a carbamoyl group, an alkoxycarbonyl group, an alkylsulfonyl group, and an alkylphosphoryl group; and most preferable group is a carbamoyl group.

[0358]

X represents preferably an electron-attracting group, and more preferably a halogen atom, an aliphatic, aryl or a heterocyclic sulfonyl group, an aliphatic, aryl or a heterocyclic acyl group, an aliphatic, aryl or a heterocyclic oxycarbonyl group, a carbamoyl group or a sulfamoyl group, and particularly preferably a halogen atom.

Among such halogen atoms, a chlorine atom, a bromine atom and an iodine atom are preferable; a chlorine atom and a bromine atom are more preferable; and a bromine atom is particularly preferable.

[0359]

Y represents preferably -C(=O)-, -SO-, or -SO<sub>2</sub>-, more

preferably -C(=O)- or -SO<sub>2</sub>-, and particularly preferably -SO<sub>2</sub>- .  
n represents 0 or 1, and preferably 1.

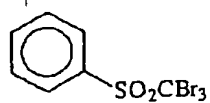
[0360]

Specific examples of compounds represented by the formula  
(H) according to the invention are described below; however,  
the invention is by no means limited thereto.

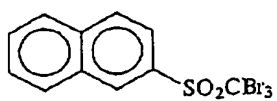
[0361]

[Formula 55]

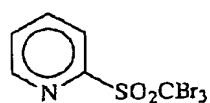
(H-1)



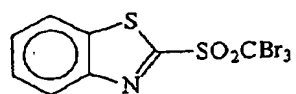
(H-2)



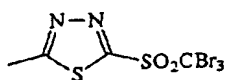
(H-3)



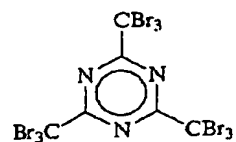
(H-5)



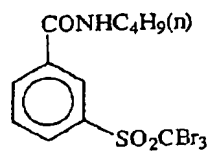
(H-6)



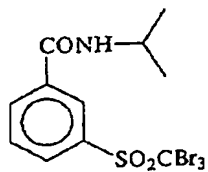
(H-7)



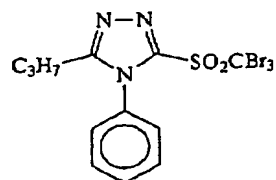
(H-8)



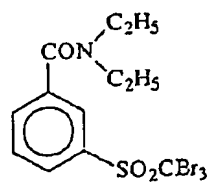
(H-9)



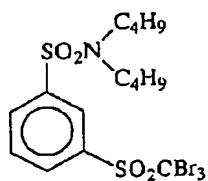
(H-10)



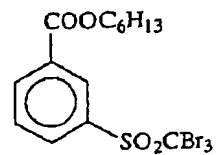
(H-11)



(H-12)



(H-13)

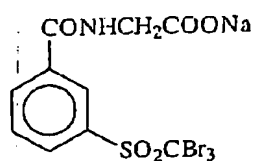




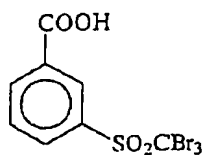
[0362]

[Formula 56]

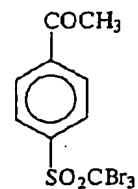
(H-14)



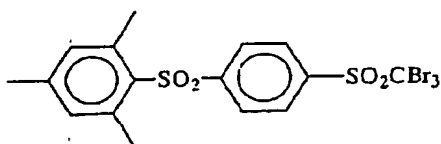
(H-15)



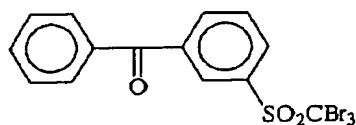
(H-16)



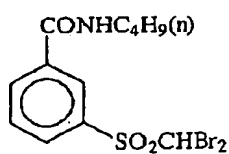
(H-17)



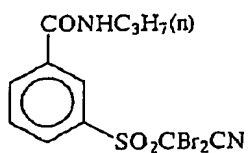
(H-18)



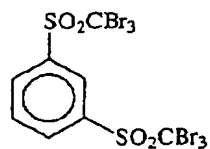
(H-19)



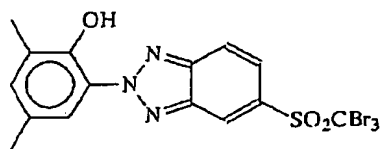
(H-20)



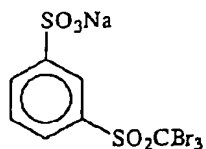
(H-21)



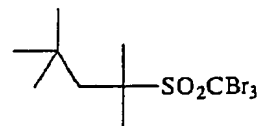
(H-22)



(H-23)



(H-24)



[0363]

The compound represented by the formula (H) according to the invention is used, based on 1 mol of non-photosensitive silver salt in the image-forming layer, preferably in a range from  $10^{-4}$  mol to 0.8 mol, more preferably from  $10^{-3}$  mol to 0.1 mol, and still more preferably from  $5 \times 10^{-3}$  mol to 0.05 mol.

Particularly, when the silver halide having a composition in which a silver iodide content is high according to the invention is used, a quantity of the compound represented by the formula (H) to be added is an important factor so as to obtain a sufficient fogging effect and the compound is most preferably used in a range from  $5 \times 10^{-3}$  mol to 0.03 mol.

[0364]

As for methods for allowing the compound represented by the formula (H) according to the invention to be contained in the photosensitive material, same methods as those described in the reduction agent are applicable.

[0365]

A melting point of the compound represented by the formula (H) is preferably 200°C or less and more preferably 170°C or less.

[0366]

As for other organic polyhalogenated materials according to the invention, compounds disclosed in patents described in paragraphs [0111] to [0112] of JP-A No. 11-65021 are cited. Particularly, organic halogen compounds represented by the formula (P) in Japanese Patent Application No. 11-87297, organic polyhalogen compounds represented by the formula (II) in JP-A No. 10-339934 and organic polyhalogen compounds described in Japanese Patent Application No. 11-205330 are preferable.

[0367]

(Description of Other Antifoggants)

As for other antifoggants, a mercury (II) salt as described in paragraph [0113] of JP-A No. 11-65021, benzoic acids as described in paragraph [0114] of P-A No. 11-65021, a salicylic acid derivative as described in JP-A No. 2000-206642, a formalin scavenger compound represented by the formula (S) in JP-A No. 2000-221634, a triazine compound related to Claim 9 of JP-A No. 11-352624, compounds represented by the formula (III) of JP-A No. 11-11791, 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene and the like are mentioned.

[0368]

As for antifoggants, stabilizers and stabilizer precursors according to the invention, those disclosed as patents as described in paragraph [0070] of JP-A No. 10-62899,

pp. 20 (line 57) to 21 (line 7) of EP-A No. 0803764A1, and compounds described in JP-A Nos. 9-281637 and 9-329864 are also mentioned.

[0369]

The photothermographic material according to the invention may contain an azolium salt for the purpose of inhibiting fogging. As for such azolium salts, compounds represented by the formula (XI) as described in JP-A No. 59-193447, compounds as described in JP-B No. 55-12581, and compounds represented by the formula (II) as described in JP-A No. 60-153039 can be cited. The azolium salt may be added in any part of the photosensitive material; however, as for a layer to be added with the azolium salt, the layer on a surface having the photosensitive layer is preferable, and the layer containing the organic silver salt is more preferable.

[0370]

Timing of adding the azolium salt may be in any step for preparing a coating solution. When the azolium salt is added to the layer containing the organic silver salt, the azolium salt may be added in any step of from preparation of the organic silver salt to preparation of a coating solution; however, the azolium salt is preferably added during a period of after the preparation of the organic silver salt to immediately before the coating. As for methods for adding the azolium salt, any

addition method, such as that in a powder state, a solution state or a fine grain dispersion state thereof, may be adopted. The azolium salt may also be added in a state of solution mixed with other additives such as a sensitizing dye, a reduction agent and a color toning agent.

[0371]

According to the invention, a quantity of the azolium salt to be added may be optional; however, it is, based on 1 mol of silver, preferably in a range from  $1 \times 10^{-6}$  mol to 2 mol, and more preferably from  $1 \times 10^{-3}$  mol to 0.5 mol.

[0372]

(Description of Other Additives)

1) Mercapto, Disulfide, and Thiones

According to the invention, for the purpose of controlling development by inhibiting or accelerating the development, improving spectral sensitization efficiency, improving storability before and after the development and the like, a mercapto compound, a disulfide compound, or a thione compound can be incorporated. Compounds as described in paragraphs [0067] to [0069] of JP-A No. 10-62899, compounds represented by the formula (I) and their specific examples as described in paragraphs [0033] to [0052] of JP-A No. 10-186572, compounds described in page 20, lines 36 to 56 of EP-A No. 0803764A1 and

Japanese Patent Application No. 11-273670. Among other things, mercapto-substituted heteroaromatic compounds are preferable.

[0373]

## 2) Color Toning Agent

In the photothermographic material according to the invention, a color toning agent is preferably added. Such color toning agents are described in paragraphs [0054] to [0055] of JP-A No. 10-62899, page 21, lines 23 to 48 of EP-A No. 0803764 A1, JP-A Nos. 2000-356317 and Japanese Patent Application No. 2000-187298. Particularly, phthalazinones (phthalazinone, phthalazinone derivatives or their metal salts, for example, 4-(1-naphthyl) phthalazinone, 6-chlorophthalazinone, 5,7-dimethoxy phthalazinone and 2,3-dihydro-1,4-phthalazinedione); combinations of phthalazinones and phthalic acids (for example, phthalic acid, 4-methylphthalic acid, 4-nitrophthalic acid, diammonium phthalate, sodium phthalate, potassium phthalate and tetrachlorophthalic acid anhydride); phthalazines (phthalazine, phthalazine derivatives or their metal salts, for example, 4-(1-naphthyl) phthalazine, 6-isopropylphthalazine, 6-t-butylphthalazine, 6-chlorophthalazine, 5,7-dimethoxyphthalazine and 2,3-dihydrophthalazine) are preferable and, in combinations with a silver halide having a composition in which a silver

iodide content is high, combinations of phthalazines and phthalic acids are particularly preferred.

[0374]

A quantity of any of the phthalazines to be added is, based on 1 mol of the organic silver salt, preferably in a range from 0.01 mol to 0.3 mol, more preferably from 0.02 mol to 0.2 mol, and particularly preferably from 0.02 mol to 0.1 mol. Such addition quantities are important factors for development acceleration which is a problem of a silver halide emulsion, according to the invention, having a composition in which a silver iodide content is high.

[0375]

### 3) Plasticizer and Lubricant

Plasticizers and lubricants employable in the photosensitive layer according to the invention are described in paragraph [0117] of JP-A No. 11-65021. Slipping agents are described in paragraphs [0061] to [0064] of JP-A No. 11-84573, and paragraphs [0049] to [0062] of Japanese Patent Application No. 11-106881.

[0376]

### 4) Dye and Pigment

From the standpoint of improving color tones, preventing

an interference fringe pattern to be generated by laser light exposure, and preventing irradiation, various types of dyes and pigments (for example, C. I. Pigment Blue 60, C. I. Pigment Blue 64, and C. I. Pigment Blue 15:6) can be used in the photosensitive layer according to the invention. These dyes and pigments are described in detail, for example, in WO98/36322, JP-A No. 10-268465, and 11-338098.

[0377]

#### 5) Ultra-hard Gradation Enhancing Agent

For the purpose of forming an ultra-hard gradation image appropriate for an application of a printing plate fabrication, an ultra-hard gradation enhancing agent is preferably added to an image-forming layer. As for such ultra-hard gradation enhancing agents, addition methods thereof, and respective quantities thereof to be added, mentioned are compounds described in paragraph [0118] of JP-A No. 11-65021, and paragraphs [0136] to [0193] of JP-A No. 11-223898, compounds represented by the formula (H), the formulas (1) to (3) and the formulas (A) and (B) in Japanese Patent Application No. 11-87297, and compounds represented by the formulas (III) to (V) in Japanese Patent Application No. 11-91652 (specifically, compounds denoted by Chemicals 21 to 24). Further, hard gradation accelerators are also described in paragraph [0102] of JP-A No. 11-65021, and paragraph [0194] to [0195] of JP-A



No. 11-223898.

[0378]

In a case in which a substance which generates formic acid or a salt thereof when decomposed is used as a strong fogging substance, the fogging substance is contained on a side having the image-forming layer containing the photosensitive silver halide, based on 1 mol of silver, in a quantity of preferably 5 millimol or less, and more preferably 1 millimol or less.

When the ultra-hard gradation enhancing agent is used in the photothermographic material according to the invention, it is preferable to use in combination an acid formed by hydration of phosphorus pentoxide or a salt thereof. As for such acids formed by hydration of phosphorus pentoxide or the salts thereof, mentioned are meta-phosphoric acid (and salts thereof), pyro-phosphoric acid (and salts thereof), ortho-phosphoric acid (and salts thereof), triphosphoric acid (and salts thereof), tetraphosphoric acid (and salts thereof), and hexameta-phosphoric acid (and salts thereof). Acids formed by hydration of phosphorus pentoxide or the salts thereof which are particularly preferably used are ortho-phosphoric acid (and salts thereof) and hexameta-phosphoric acid (and salts thereof). Specific examples of the salts include sodium ortho-phosphate, sodium dihydrogen ortho-phosphate, sodium hexameta-phosphate and ammonium hexameta-phosphate.

A quantity of the acid formed by hydration of phosphorus pentoxide or the salt thereof to be used (in terms of a coated quantity based on 1 m<sup>2</sup> of the photosensitive material) may be a desired quantity, depending on properties of sensitivity, fog, and the like; however, it is preferably in a range from 0.1 mg/m<sup>2</sup> to 500 mg/m<sup>2</sup>, and more preferably from 0.5 mg/m<sup>2</sup> to 100 mg/m<sup>2</sup>.

[0379]

(Preparation and Application of Coating Solution)

A temperature at which the coating solution for the image-forming layer according to the invention is prepared is preferably in a range from 30°C to 65°C, more preferably from 35°C to less than 60°C, and still more preferably from 35°C to 55°C. It is also preferable that the temperature of the coating solution for the image-forming layer immediately after the polymer latex is added thereto is maintained in a range from 30°C to 65°C.

[0380]

## 2. Layer Composition and Other Composition Components

[0381]

The photothermographic material according to the invention may be a "one-side type" which has an image-forming

layer only on one side of a support, or a "double-side type" which has the image-forming layer on both sides thereof.

(Double-side-type photothermographic material)

A double-side-type photothermographic material according to the invention can be used in an image-forming method in which an X-ray image is recorded by using an X-ray intensifying screen.

Preferably used in such image-forming method is a photothermographic material in which, after exposure with an X-ray intensifying screen and a monochromatic light which has a same wavelength as that of a main luminescent peak of the X-ray intensifying screen and a half bandwidth of  $15 \pm 5$  nm, and thermal development, an image is obtained by removing the image-forming layer on the surface opposite to the exposed surface, and the exposure quantity necessary for the density of the image to become the minimum density plus 0.5 is 0.005 to 0.07 lux-second.

The image-forming method which uses this double-side type preferably comprises at least the following steps of:

(a) obtaining an image-forming combined system by providing the photothermographic material between a pair of X-ray intensifying screens;

(b) placing a subject between the combined system and an X-ray source;

(c) irradiating an X-ray having an energy level of from

25 kVp to 125 kVp on the subject;

(d) retrieving the photothermographic material from the combined system; and

(e) heating the thus-retrieved photothermographic material at a temperature of from 90°C to 180°C.

[0382]

The photothermographic material to be used in the combined system according to the invention is preferably prepared such that an image to be obtained by exposing the photosensitive material by an X-ray in a stepwise manner and, then, thermally developing it has a characteristic curve, being constructed on a crossed coordinates having same unit lengths of coordinate axes denoting optical density (D) and exposure quantity (logE) respectively, in which an average gamma ( $\gamma$ ) obtained by a point of a minimum density (Dmin) plus density 0.1 and a point of a minimum density (Dmin) plus density 1.2 is in a range from 0.5 to 0.9, and an average gamma ( $\gamma$ ) obtained by a point of a minimum density (Dmin) plus density 1.2 and a point of a minimum density (Dmin) plus density 1.6 is in a range from 3.2 to 4.0. When the photothermographic material having the characteristic curve is used in an X-ray photographing system, an X-ray image having excellent photographic characteristics in which a foot part of the characteristic curve is extremely extended and also a gamma value in an intermediate density part is high can be

obtained. By these photographic characteristics, there is a merit in that depiction of a low density area, for example, a mediastinum area, or cardioshadowgraph which is low in X-ray transmission quantity becomes enhanced and, further, an image of a lung field which is subjected to a large X-ray exposure quantity comes to have a density which allows the lung field to be easily recognized and, also, comes to have a favorable contrast.

[0383]

The photothermographic material having such favorable characteristic curve as described above can easily be produced by, for example, a method in which an image-forming layer on each side is constituted by two or more layers which are different in sensitivity from each other. Particularly, it is preferable to form the image-forming layer by using a high-speed emulsion having as an upper layer and an emulsion having photographic characteristics of low speed and hard tone as a lower layer. When the image-forming layer comprising such two layers as described above is used, a difference in speeds between silver halide emulsions of the two layers is in a range from 1.5 time to 20 times, and preferably from 2 times to 15 times. Further, a ratio of quantities of emulsions to be used in forming respective layers differs depending on differences in speeds and covering powers of the emulsions to be used. Ordinarily,

as the difference in speeds of the emulsions to be used becomes larger, the ratio of quantities thereof becomes lower. For example, when the difference in speeds is two times, a preferable ratio of emulsions to be used, namely, a high-speed emulsion to a low-speed emulsion, is adjusted to be in a range from 1:20 to 1:50 in terms of silver quantity on condition that covering powers of respective emulsions are same with each other.

[0384]

Emulsion sensitizing methods, various types of additives, constituting materials and the like to be used in preparation of the photothermographic material according to the invention are not particularly limited. For example, various types of techniques as described in, for example, JP-A Nos. 2-68539, 2-103037, and 2-115837 can be utilized.

[0385]

As for techniques of cross-over cut (for double-side-type photosensitive material) and antihalation (for single-side-type material), dyes, dyes and mordants as described in JP-A No. 2-68539, from page 13, left lower column, line 1 to page 14, left lower column, line 9 can be used.

[0386]

Next, a fluorescent intensifying screen (radiation

intensifying screen) will be described. The radiation intensifying screen comprises, as a basic structure, a support, and a phosphor layer formed on one side of the support. The phosphor layer is a layer in which a phosphor is dispersed in a binder. Further, a transparent protective layer is ordinarily provided on a surface of the phosphor layer opposite to the support (a surface thereof on a side not facing the support) to protect the phosphor layer from a chemical change in quality or a physical impact.

[0387]

Examples of preferable phosphors according to the invention include a tungstate-type phosphor (for example,  $\text{CaWO}_4$ ,  $\text{MgWO}_4$ , or  $\text{CaWO}_4:\text{Pb}$ ), a terbium-activated rare earth metal oxysulfide-type phosphor (for example,  $\text{Y}_2\text{O}_2\text{S}:\text{Tb}$ ,  $\text{Gd}_2\text{O}_2\text{S}:\text{Tb}$ ,  $\text{La}_2\text{O}_2\text{S}:\text{Tb}$ ,  $(\text{Y},\text{Gd})_2\text{O}_2\text{S}:\text{Tb}$ ,  $(\text{Y},\text{Gd})\text{O}_2\text{S}:\text{Tb},\text{Tm}$ ), a terbium-activated rare earth metal phosphate-type phosphor (for example,  $\text{YPO}_4:\text{Tb}$ ,  $\text{GdPO}_4:\text{Tb}$ , or  $\text{LaPO}_4:\text{Tb}$ ), a terbium-activated rare earth element oxyhalogenide type phosphor (for example,  $\text{LaOBr}:\text{Tb}$ ,  $\text{LaOBr}:\text{Tb},\text{Tm}$ ,  $\text{LaOCl}:\text{Tb}$ ,  $\text{LaOCl}:\text{Tb},\text{Tm}$ ,  $\text{GdOBr}:\text{Tb}$ , or  $\text{GdOCl}:\text{Tb}$ ) and a thulium-activated rare earth element oxyhalogenide type phosphor (for example,  $\text{LaOBr}:\text{Tm}$ , or  $\text{LaOCl}:\text{Tm}$ ). a barium sulfate-type phosphor (for example,  $\text{BaSO}_4:\text{Pb}$ ,  $\text{BaSO}_4:\text{Eu}^{2+}$ , or  $(\text{Ba},\text{Sr})\text{SO}_4:\text{Eu}^{2+}$ ), a divalent europium-activated alkaline earth metal phosphate-type phosphor (for example,  $(\text{Ba}_2\text{PO}_4)_2:\text{Eu}^{2+}$ , or

( $\text{Ba}_2\text{PO}_4)_2:\text{Eu}^{2+}$ ), a divalent europium-activated alkaline earth metal fluorohalogenide-type phosphor (for example,  $\text{BaFCl}:\text{Eu}^{2+}$ ,  $\text{BaFBr}:\text{Eu}^{2+}$ ,  $\text{BaFCl}:\text{Eu}^{2+},\text{Tb}$ ,  $\text{BaFBr}:\text{Eu}^{2+},\text{Tb}$ ,  $\text{BaF}_2\cdot\text{BaCl}\cdot\text{KCl}:\text{Eu}^{2+}$ , or  $(\text{Ba},\text{Mg})\text{F}_2\cdot\text{BaCl}\cdot\text{KCl}:\text{Eu}^{2+}$ ), an iodide-type phosphor (for example,  $\text{CsI}:\text{Na}$ ,  $\text{CsI}:\text{TI}$ , or  $\text{NaI},\text{KI}:\text{TI}$ ), sulfide-type phosphor (for example,  $\text{ZnS}:\text{Ag}$  ( $\text{Zn},\text{Cd}$ ) $\text{S}:\text{Ag}$ , ( $\text{Zn},\text{Cd}$ ) $\text{S}:\text{Cu}$ , or ( $\text{Zn},\text{Cd}$ ) $\text{S}:\text{Cu},\text{Al}$ ), and a hafnium phosphate-type phosphor (for example,  $\text{HfP}_2\text{O}_7:\text{Cu}$ ). However, the invention is by no means limited thereto and any types of phosphors can be used, so long as they can emit visible light or light in a near-ultraviolet region.

[0388]

The fluorescent intensifying screen according to the invention is preferably filled with the phosphor in a gradient diameter structure. Particularly, it is preferable that a phosphor grain having a large diameter is applied to a surface protective layer side and a phosphor grain having a small diameter to a support side. It is preferable that the small diameter is in a range from 0.5  $\mu\text{m}$  to 2.0  $\mu\text{m}$  while the large diameter is in a range from 10  $\mu\text{m}$  to 30  $\mu\text{m}$ .

[0389]

(Single-side-type photothermographic material)

The single-side-type photothermographic material according to the invention is preferably used in particular



as a photosensitive material for mammography.

It is important that the single-side-type photothermographic material according to the invention is designed such that contrast of the image to be obtained falls in an appropriate range.

[0390]

Next, a method for obtaining the characteristic curve of the photothermographic material according to the invention will be described. In the mammography, exposure is ordinarily performed by using an Mo target tube which emits a low potential X-ray. However, for practical use, a characteristic curve obtained by a method in which X-ray exposure quantity is changed by using an X-ray emitted from a tungsten-target tube as a radiation source by means of a distance method is not substantially different from that obtained by the above-described method, so long as the intensifying screen comprising a phosphor comprising  $Gd_2O_3S:Tb$  is used.

[0391]

Specifically, when measurements were performed this time, a method in which the X-ray emitted from the tungsten-target tube which was operated at 50 kVp generated by a three-phase power supply was allowed to transmit an aluminum plate having a thickness of 3 mm was used. A commercially available UM-Fine

screen and a photosensitive material to be measured were allowed to be in contact with each other and, then, inserted in an ECMA cassette (trade name; manufacture by Fuji Photo Film Co., Ltd.). An X-ray tube, a cassette upper lid, a film, and a screen were aligned in the stated order and were subjected to an X-ray exposure. Exposure was conducted in a stepwise manner at a width of  $\log E = 0.15$  by changing the X-ray exposure quantities by means of the distance method.

[0392]

An exposed film is thermally developed under a predetermined condition and, then, density of the thus-developed film is measured. Thereafter, a characteristic curve is obtained by plotting a logarithm of an exposure quantity of an irradiation ray in abscissa against an optical density in ordinate. A contrast can be obtained from an inclination of a straight line (tangent  $\theta$  when an angle of the straight line to abscissa is represented by  $\theta$ ) connected by two density points of fog plus 0.25 and fog plus 2.0.

[0393]

Next, a measuring method of sensitivity of the photosensitive material will be described. A monochromatic light having a same wavelength as that of a main luminescent peak of the X-ray intensifying screen to be used is used. As

for methods for obtaining such light, a method which uses a filter system combined with an interference filter can be used. By this method, although depending on combinations of interference filters, ordinarily, light having a necessary exposure quantity and a half bandwidth of  $15\pm 5$  nm can easily be obtained.

[0394]

The photosensitive material placed 1 m apart from the light source is exposed for one second through a step-wedge of a neutral filter by using the above-described light as the light source in which luminance is accurately measured by a luminometer which has previously been appropriately calibrated. After thermal development is performed, the density of the thus-obtained image is measured, and an exposure quantity which can obtain fog plus density 0.5 is measured to determine sensitivity of the photosensitive material. The sensitivity can be denoted in terms of lux-second.

[0395]

The sensitivity of the photothermographic material for mammography according to the invention is preferably in a range from 0.01 lux-second to 0.07 lux-second. The contrast thereof is preferably in a range from 3.0 to 5.0.

[0396]

Next, an intensifying screen for mammography according to the invention will be described in detail. The X-ray intensifying screen of a photographing combined system for mammography for one purpose of the invention required high resolution compared with that for chest-area diagnosis or the like. Therefore, a commercially available ordinary X-ray intensifying screen for mammography is prepared by coloring a phosphor layer thereof to enhance the resolution. However, such coloring prevents light emitted by the X-ray absorbed by the phosphor present far from a surface to which the X-ray is incident from being effectively drawn out. For the X-ray intensifying screen according to the invention, it is required to provide a screen in which the phosphor capable of sufficiently absorbing the X-ray without substantially coloring the phosphor layer is applied to obtain a necessary high sharpness.

[0397]

In order to achieve a target of such a screen as described above, a grain size of the phosphor is preferably a given size or less. As for the measuring methods of the size of the phosphor, mentioned are, for example, a coulter-counter method, and an electron microscopy. An average sphere-equivalent diameter of such phosphor sizes is preferably in the range of from 1  $\mu\text{m}$  to 5  $\mu\text{m}$ , and more preferably from 1  $\mu\text{m}$  to 4  $\mu\text{m}$ . Although

these ranges are not important for a conventional screen for mammography which colors the phosphor layer, they are important for the screen according to the invention.

[0398]

Further, in order to enhance sharpness with the screen, it is preferable that a rate of a binder in a weight ratio of the binder to the phosphor is small. The weight ratio of the binder to the phosphor is preferably in a range from 1/50 to 1/20, and more preferably from 1/50 to 1/25.

[0399]

As for binders, known binders as described in JP-A No. 6-75097, from page 4, right column, line 45 to page 5, left column, line 10 can be used, thermoplastic elastomers having a softening temperature or melting point of from 30°C to 150°C are preferably used each individually or in combinations with other binder polymers. In such a screen having a small quantity of the binder for enhancing the sharpness as in the invention, durability thereof is liable to be deteriorated and, accordingly, it is necessary to select a binder which can withstand such deterioration. To solve such a problem, it is preferable to select a binder having a sufficient flexibility. Further, it is preferable to incorporate, for example, a plasticizer, in the phosphor layer. Examples of thermoplastic elastomers

include polystyrene, polyolefin, polyurethane, polyester, polyamide, polybutadiene, ethylene-vinyl acetate, natural rubber, fluororubber, polyisoprene, chlorinated polyethylene, styrene-butadiene rubber, and silicone rubber, in which polyurethane is particularly preferred. It is also important to select an appropriate binder or undercoat of the phosphor layer; an acrylic binder is preferably used.

[0400]

Further, it is preferable that a surface protective layer of the screen is as thin as possible within a range in which scratch resistance and stain resistance are secured; thickness of the surface protective layer thereof is preferably in a range from 2  $\mu\text{m}$  to 7  $\mu\text{m}$ .

[0401]

A material for the surface protective layer can be prepared by laminating PET (particularly stretched type), PEN, nylon and the like one on top of another. Further, it is also preferable from the standpoint of stain resistance that the surface protective layer is formed by applying a solution in which a fluorocarbon resin is dissolved in a solvent. A preferred embodiment of the fluorocarbon resin is described in detail in JP-A No. 6-75097, page 6, from left column, 4 line to right column, 43 line. As for other resins which can form the surface

protective layer in such a solvent-application manner as described above, mentioned are a polyurethane resin, a polyacrylic resin, a cellulose derivative, polymethyl methacrylate, a polyester resin, an epoxy resin and the like other than a fluorocarobon resin.

[0402]

It is also important that a filling rate of the phosphor is sufficiently high for obtaining the screen having a high sensitivity and high sharpness. Specifically, a volume filling rate of the phosphor is preferably in a range from 60% to 80%, and more preferably from 65% to 80%. In order to maintain the volume filling rate by the phosphor of such fine grain according to the invention to be high, a process for compressing the phosphor layer as described in JP-A No. 6-75097, from page 4, right column, line 29 to page 6, left column, line 1 is favorably used.

[0403]

It is preferable that the phosphor according to the invention is substantially  $\text{Gd}_2\text{O}_3\text{S:Tb}$ . The term "substantially" as used in the above description is intended to mean that a main component of the phosphor is  $\text{Gd}_2\text{O}_3\text{S:Tb}$  and, also, 1 to 9% of an additive for enhancing performance, silica for modifying the surface, or the like can favorably be used. Further, Y,

La, or Lu can simultaneously be used replacing 10 to 90% of Gd.

[0404]

Ordinarily, density of the phosphor is preferably high to effectively absorb the X-ray. As for phosphors which exhibit a preferable absorption of the X-ray emitted from a radiation source for use in the mammography, not only  $\text{Gd}_2\text{O}_2\text{S:Tb}$ , but also  $\text{YTaO}_4$  and a derivative thereof prepared by adding any one of various types of activating agents thereto as a luminescence center,  $\text{CaWO}_4$ , and  $\text{BaFBr:Eu}$  are mentioned.

[0405]

(Combination with Ultraviolet Fluorescent Screen)

As for image-forming methods using photothermographic material according to the invention, a method in which images are formed in combination with a phosphor having a main peak at preferably 400 nm or less, and more preferably 380 nm or less can be used. The double-side-type photosensitive material and the single-side-type photosensitive material can each individually be used as a combined system. As for such screens each having a main peak at 400 nm or less, screens as described in, for example, JP-A No. 6-11804, and WO93/01521 can be used; however, the present invention is by no means limited thereto. As for techniques of crossover-cut of the ultraviolet ray (for



double-side-type photosensitive material) and antihalation (for single-side-type photosensitive material), those as described in JP-A No. 8-76307 can be used. As for ultraviolet ray-absorbing agents, a dye as described in Japanese Patent Application No. 2002-320809 is particularly preferred.

[0406]

The photothermographic material according to the invention may contain a non-image-forming layer in addition to the image-forming layer. The non-image-forming layer can be classified according to its position as follows; (a) a surface protective layer formed on the image-forming layer (on a farther side from a support), (b) an intermediate layer formed between any two of a plurality of image-forming layers or between the image-forming layer and the protective layer, (c) an undercoat layer formed between the image-forming layer and the support, and (d) a back layer formed on a side opposite to the image-forming layer.

[0407]

Further, a layer acting as an optical filter can be formed in the photosensitive material as a layer classified in the above-described (a) or (b). An antihalation layer is formed in the photosensitive material as a layer classified in the above-described (c) or (d).

[0408]

1) Surface Protective Layer

The photothermographic material according to the invention may have a surface protective layer for the purpose of preventing adhesion of the image-forming layer and the like. The surface protective layer may be of a single layer or of a plurality of layers. Such surface protective layers are described in paragraphs [0119] to [0120] of JP-A No. 11-65021, and Japanese Patent Application No. 2000-171936.

[0409]

As for binders for the surface protective layer according to the invention, gelatin is preferably used, and polyvinyl alcohol (PVA) is also preferably used solely or in combination with gelatin. As for gelatin, inert gelatin (for example, Nitta Gelatin 750), phthalated gelatin (for example, Nitta Gelatin 801) and the like can be used.

[0410]

As for PVA, those described in paragraphs [0009] to [0020] of JP-A No. 2000-171936 can be cited. PVA-105 as a completely saponified PVA, PVA-205 and PVA-335 as partly saponified PVA, and MP-203 as a modified polyvinyl alcohol (these are manufactured by Kuraray Co., Ltd.) are preferably mentioned.

[0411]

A quantity (based on 1 m<sup>2</sup> of the support) of polyvinyl alcohol to be coated of the protective layer (per one layer) is preferably in a range from 0.3 g/m<sup>2</sup> to 4.0 g/m<sup>2</sup>, and more preferably from 0.3 g/m<sup>2</sup> to 2.0 g/m<sup>2</sup>.

[0412]

A quantity (based on 1 m<sup>2</sup> of the support) of the entire binder (inclusive of water-soluble polymer and latex polymer) to be coated of the surface protective layer (per one layer) is preferably in a range from 0.3 g/m<sup>2</sup> to 5.0 g/m<sup>2</sup>, and more preferably from 0.3 g/m<sup>2</sup> to 2.0 g/m<sup>2</sup>.

[0413]

## 2) Antihalation Layer

In the photothermographic material according to the invention, an antihalation layer can be formed at the farther side from an exposure light source relative to the image-forming layer. Such antihalation layers are described, for example, in paragraphs [0123] to [0124] of JP-A No. 11-65021, JP-A Nos. 11-223898, 9-230531, 10-36695, 10-104779, 11-231457, 11-352625, and 11-352626.

[0414]

The antihalation layer contains an antihalation dye having an absorption in an exposure wavelength. When such exposure wavelength is in an infrared region, a dye absorbing an infrared ray may be used; on this occasion, the dye having no absorption in a visible wavelength region is preferred.

[0415]

When antihalation is performed by using a dye having absorption in the visible wavelength region, it is preferred that color of the dye does not remain substantially after an image is formed, a device to decolorize the dye by heat in thermal development is used and a thermally decolorizable dye and a base precursor are added to the non-image-forming layer to allow the resultant non-image-forming layer to function as an antihalation layer. Such techniques are described in JP-A No. 11-231457 and the like.

[0416]

A quantity of the decolorizable dye to be added is determined depending on applications of the dye. Ordinarily, the decolorizable dye is used in such a quantity that an optical density (absorbance) measured at the objective wavelength exceeds 0.1. The optical density is preferably in a range from 0.2 to 2. A quantity of the decolorizable dye for obtaining the above-described optical density is ordinarily in a range

from about 0.001 g/m<sup>2</sup> to about 1 g/m<sup>2</sup>.

[0417]

When the dye is decolorized in such a way, the optical density after thermal development is performed can be lowered to 0.1 or less. Two or more types of decolorizable dyes may be used in combination in a thermally decolorizable-type recording material or in the photothermographic material. In a similar way, two or more types of base precursors may be used in combination.

[0418]

In the thermal decolorization using such a decolorizable dye and base precursor as described above, it is preferable from the viewpoint of thermal decolorization properties and the like that a substance (for example, diphenylsulfone, or 4-chlorophenyl (phenyl) sulfone) which decreases a melting point by 3°C or more when mixed with the base precursor as described in JP-A No. 11-352626 is simultaneously used.

[0419]

### 3) Back Layer

Back layers applicable to the invention are described in paragraphs [0128] to [0130] of JP-A No. 11-65021.

[0420]

According to the invention, a coloring agent having an absorption maximum in the wavelength region of from 300 nm to 450 nm can be added for the purpose of improving silver color tone and improving change of image over time. Such coloring agents are described in, for example, JP-A Nos. 62-210458, 63-104046, 63-103235, 63-208846, 63-306436, 63-314535, and 1-61745, and Japanese Patent Application No. 11-276751. The coloring agents are each added ordinarily in a range from 0.1 mg/m<sup>2</sup> to 1 g/m<sup>2</sup>. As a layer for such addition, a back layer provided on a side opposite to the image-forming layer is preferred.

[0421]

#### 4) Matting Agent

According to the invention, it is preferred to add a matting agent to the surface protective layer and the back layer for improving transportation properties. Such matting agents are described in paragraphs [0126] to [0127] of JP-A No. 11-65021.

A quantity of the matting agent to be added is, based on 1 m<sup>2</sup> of the photosensitive material, preferably in a range from 1 mg/m<sup>2</sup> to 400 mg/m<sup>2</sup>, and more preferably from 5 mg/m<sup>2</sup> to 300 mg/m<sup>2</sup>.

[0422]

Further, as a matting degree of an emulsion surface, any degree is permissible so far as a so-called star dust-like defect in which a small blank area is generated in an image portion to cause a light leakage does not occur; however, a Beck's degree of smoothness is in the range preferably of from 30 seconds to 2000 seconds, and particularly preferably from 40 seconds to 1500 seconds. The Beck's degree of smoothness can easily be obtained in accordance with TAPPI Standard Method T479 and "Testing Method for Smoothness of Paper and Paperboard by Beck's Tester" according to JIS P8119.

[0423]

According to the invention, the Beck's degree of smoothness as a matting degree for the back layer is preferably in a range from 10 seconds to 1200 seconds, more preferably from 20 seconds to 800 seconds, and still more preferably from 40 seconds to 500 seconds.

[0424]

According to the invention, the matting agent is preferably contained in an outermost surface layer, a layer functioning as the outermost surface layer, or a layer in a neighborhood of the outer surface layer which functions as the so-called protective layer.

[0425]

#### 5) Polymer Latex

A polymer latex can be added in the surface protective layer or the back layer according to the invention.

Such polymer latices are described in, for example, "*Synthetic Resin Emulsion*", compiled by Taira Okuda and Hiroshi Inagaki, Kobunshi Kankokai (Polymer Publishing) (1978), "*Application of Synthesized Latex*", compiled by Takaaki Sugimura, Yasuo Kataoka, Soichi Suzuki and Keiji Kasahara, Kobunshi Kankokai (Polymer Publishing) (1993), and Soichi Muroi, "*Chemistry of Synthesized Latex*", Kobunshi Kankokai (Polymer Publishing) (1970). Specific examples of the polymer latices include a latex of a methyl methacrylate (33.5% by mass)/ethyl acrylate (50% by mass)/methacrylic acid (16.5% by mass) copolymer, a latex of a methyl methacrylate (47.5% by mass)/butadiene (47.5% by mass)/itaconic acid (5% by mass) copolymer, a latex of an ethyl acrylate/methacrylic acid copolymer, a latex of a methyl methacrylate (58.9% by mass)/2-ethylhexyl acrylate (25.4% by mass)/styrene (8.6% by mass)/2-hydroxyethyl metacrylate (5.1% by mass)/acrylic acid (2.0% by mass) copolymer, and a latex of a methyl methacrylate (64.0% by mass)/styrene (9.0% by mass)/butyl acrylate (20.0% by mass)/2-hydroxyethyl metacrylate (5.0% by mass)/acrylic acid (2.0% by mass) copolymer.



[0426]

A quantity of the polymer latex to be added in the surface protective layer or the back layer is, based on an entire binder (inclusive of water-soluble polymer and latex polymer), preferably in a range from 10% by mass to 90% by mass, and particularly preferably from 20% by mass to 80% by mass.

[0427]

#### 6) Film Surface pH

In the photothermographic material according to the invention, a film surface pH before the thermal development is preferably 7.0 or less, and more preferably 6.6 or less. A lower limit is not particularly restricted but is approximately 3. A most preferable pH is in a range from 4 to 6.2.

[0428]

For adjusting the film surface pH, it is preferred from the viewpoint of lowering the film surface pH that an organic acid such as a phthalic acid derivative, a non-volatile acid such as sulfuric acid or a volatile base such as ammonia is used. Particularly, ammonia is preferable for achieving a low film surface pH, because ammonia is particularly apt to be vaporized and can be removed during a coating step or before being subjected to the thermal development. Further, it is also preferred that a non-volatile base such as sodium hydroxide,

potassium hydroxide or lithium hydroxide is used with ammonia in combination. Furthermore, measurement methods of the film surface pH are described in paragraph [0123] of Japanese Patent Application No. 11-87297.

[0429]

#### 7) Film Hardening Agent

A film hardening agent may be used in each of the image-forming layer, the protective layer, the back layer and the like according to the invention.

Examples of such film hardening agents are found in various methods described in T. H. James, *The Theory of the Photographic Process*, 4th edition, Macmillan Publishing Co., Inc., pp. 77 to 87 (1977). In addition to compounds such as chrome alum, sodium salt of 2,4-dichloro-6-hydroxy-s-triazine, N,N-ethylene bis(vinylsulfone acetamide) and N,N-propylene bis(vinylsulfone acetamide), polyvalent metal ions described in the above-cited reference, page 78 and the like, polyisocyanates as described in USP No. 4,281,060, JP-A No. 6-208193 and the like, epoxy compounds as described in USP No. 4,791,042, and vinyl sulfone-type compounds as described in JP-A No. 62-89048 are preferably used.

[0430]

The film hardening agent is added as a solution. Timing

of adding such film hardening agent solution into the coating solution for the protective layer is in a period of from 180 minutes before coating to immediately before coating, and preferably in a period of from 60 minutes before coating to 10 seconds before coating; however, mixing methods and mixing conditions for the film hardening agent solution are not particularly limited so far as the effects according to the invention are sufficiently realized.

[0431]

Specific examples of mixing methods include a mixing method using a tank in which an average staying time calculated from an addition flow rate and a feeding flow rate to a coater is adjusted to be a desired time, and a mixing method using a static mixer described in N. Harnby, M. F. Edwards and A. W. Nienow, *Techniques of Mixing Liquids*, translated by Koji Takahashi, Nikkan Kogyo Newspaper (1989), Chapter 8 and the like.

[0432]

#### 8) Surfactant

Surfactants according to the invention are described in paragraph [0132] of JP-A No. 11-65021.

According to the invention, fluorine-type surfactants may preferably be used. Specific preferred examples of

fluorine-type surfactants include compounds as described in, for example, JP-A Nos. 10-197985, 2000-19680, and 2000-214554. Also, polymeric fluorine-type surfactants as described in JP-A 9-281636 are preferably used. According to the invention, the fluorine-type surfactants as described in Japanese Patent Application No. 2000-206560 are particularly preferably used.

[0433]

#### 9) Antistatic agent

Further, according to the invention, an antistatic layer containing various types of known metal oxides or electrically conductive polymers may be provided. The antistatic layer may concurrently function as the above-described undercoat layer, back layer, surface protective layer or the like, or may separately be provided from these layers. The antistatic layer may adopt techniques as described in paragraphs [0135] of JP-A No. 11-65021, JP-A Nos. 56-143430, 56-143431, 58-62646, and 56-120519, paragraphs [0040] to [0051] of JP-A No. 11-84573, USP. No. 5,575,957, and paragraphs [0078] to [0084] of JP-A No. 11-223898.

[0434]

#### 10) Support

As for transparent supports, polyester, particularly, polyethylene terephthalate, which has been subjected to a

thermal treatment in the temperature range of from 130°C to 185°C in order to relax residual internal stress in the film generated when being biaxially stretched and to eliminate the strain of thermal contraction generated when subjected to the thermal treatment, is preferably used.

[0435]

As for supports of the photothermographic material to be used in combination with an ultraviolet luminescent screen, PEN is favorably used. However, the invention is by no means limited thereto. In regard PEN, a polyethylene-2,6-naphthalate is preferred. As for the polyethylene-2,6-naphthalate used herein, any substance is permissible, so long as a recurring structural unit thereof is substantially constituted by an ethylene-2,6-naphthalene-dicarboxylate unit; examples of such polyethylene-2,6-naphthalates include not only an uncopolymerized polyethylene-2,6-naphthalene-dicarboxylate, but also a copolymer thereof in which 10% or less, and more preferably 5% or less of the recurring structural units therein is modified with other components, and a mixture or composition containing other polymers.

[0436]

The polyethylene-2,6-naphthalate is synthesized by

bonding naphthalene-2,6-dicarboxylic acid or a functional derivative, and ethylene glycol or a functional derivative in the presence of a catalyst under an appropriate reaction condition; however, examples of the polyethylene-2,6-naphthalates according to the invention also include a copolymerized or mixed polyester which is prepared by adding thereto one or more types of appropriate third components (modifying agent) before polymerization of the polyethylene-2,6-naphthalate is completed. Examples of the appropriate third components include a compound having a divalent ester-forming functional group, for example, a dicarboxylic acid such as oxalic acid, adipic acid, phthalic acid, isophthalic acid, terephthalic acid, naphthalene-2,7-dicarboxylic acid, succinic acid or diphenylether-dicarboxylic acid, a lower alkylester thereof, an oxycarbonic acid such as p-oxybenzoic acid or p-oxyethoxybenzoic acid, a lower alkylester thereof, and a dihydric alcohol such as propylene glycol or trimethylene glycol. As for such polyethylene-2,6-naphthalates or modified polymers thereof, for example, those prepared by blocking at least one of a terminal hydroxyl group and carboxylic group thereof by monofunctional compound such as benzoic acid, benzoylbenzoic acid, benzyloxybenzoic acid or methoxypolyalkylene glycol, and those modified by a very small amount of a three- or four-functional ester-forming compound such as glycerin or

pentaerythritol within a range in which a linear copolymer is substantially obtained are permissible.

[0437]

In case of the photothermographic materials for medical diagnosis use, the transparent support may be colored with a blue dye (for example, Dye-1 as described in JP-A No. 8-240877) or may not be colored.

Specific examples of the supports are described in paragraphs [0134] of JP-A No. 11-65021.

[0438]

In the supports, undercoat techniques of a water-soluble polyester as described in JP-A No. 11-84574, a styrene-butadiene copolymer as described in JP-A No. 10-186565, vinylidene chloride copolymers as described in JP-A No. 2000-39684, paragraphs [0063] to [0080] of Japanese Patent Application No. 11-106881 and the like are preferably applied.

[0439]

#### 11) Other Additives

To the photothermographic material, an anti-oxidant, a stabilizing agent, a plasticizer, an ultraviolet ray-absorbing agent or a covering aid may further be added. A solvent as described in paragraph [0133] of JP-A No. 11-65021 may be added.

Various types of these additives are added either to the image-forming layer or to the non-image-forming layer. In regard to those additives, WO98/36322, EP-A No. 803764A1, JP-A Nos. 10-186567 and 10-18568 and the like can be referred.

[0440]

#### 12) Coating Method

The photothermographic material according to the invention may be applied by any method. Various types of coating operations may be used; and specific examples thereof include extrusion coating, slide coating, curtain coating, dip coating, knife coating, flow coating, and extrusion coating using such a kind of hopper as described in USP No. 2,681,294. Extrusion coating or slide coating as described in Stephen F. Kistler and Peter M. Schweizer, Liquid Film Coating, Chapman & Hall, pp. 399 to 536 (1997) is preferably used. Particularly, slide coating is preferably used therebetween.

[0441]

Examples of shapes of slide coaters to be used for slide coating are described in the above-cited book, pp. 427, FIG. 11b-1. Further, as desired, two or more layers can simultaneously be coated by methods described in the above-cited book, pp. 399 to 536, USP No. 2,761,791 and BP-A No. 837,095.



[0442]

It is preferable that a coating solution for the organic silver salt-containing layer according to the invention is a so-called thixotropic fluid. Techniques related to this fluid can be referred to JP-A No. 11-52509.

In regard to the coating solution for the organic silver salt-containing layer according to the invention, a viscosity thereof at the shearing velocity of  $0.1 \text{ S}^{-1}$  is preferably in a range from 400 mPa·s to 100,000 mPa·s, and more preferably from 500 mPa·s to 20,000 mPa·s.

Further, a viscosity at the shearing velocity of  $1000 \text{ S}^{-1}$  is preferably in a range from 1 mPa·s to 200 mPa·s, and more preferably from 5 mPa·s to 80 mPa·s.

[0443]

### 13) Wrapping material

It is preferable that the photothermographic material according to the invention is hermetically packed by a wrapping material having at least one of a low oxygen transmittance and a low moisture transmittance in order to prevent photographic properties from being deteriorated at the time of storage before being used, or prevent a product using the photothermographic material from being curled or curly deformed when the product is in roll form. The oxygen transmittance at  $25^{\circ}\text{C}$  is preferably  $50 \text{ ml/atm/m}^2\cdot\text{day}$  or less, more preferably  $10 \text{ ml/atm/m}^2\cdot\text{day}$  or

less, and still more preferably 1.0 ml/atm/m<sup>2</sup>·day or less. The moisture transmittance is preferably 10 g/atm/m<sup>2</sup>·day or less, more preferably 5 g/atm/m<sup>2</sup>·day or less, and still more preferably 1 g/atm/m<sup>2</sup>·day or less. Specific examples of employable wrapping materials in which at least one of the oxygen transmittance and the moisture transmittance is low include those as described in JP-A Nos. 8-254793 and 2000-206653.

[0444]

#### 14) Other Employable Techniques

As for techniques employable in the photothermographic materials according to the invention, techniques described in the following references are further cited: EP-A Nos. 803764A1, and 883022A1, WO98/36322, JP-A Nos. 56-62648, 58-62644, 9-43766, 9-281637, 9-297367, 9-304869, 9-311405, 9-329865, 10-10669, 10-62899, 10-69023, 10-186568, 10-90823, 10-171063, 10-186565, 10-186567, from 10-186569 to 10-186572, 10-197974, 10-197982, 10-197983, from 10-197985 to 10-197987, 10-207001, 10-207004, 10-221807, 10-282601, 10-288823, 10-288824, 10-307365, 10-312038, 10-339934, 11-7100, 11-15105, 11-24200, 11-24201, 11-30832, 11-84574, 11-65021, 11-109547, 11-125880, 11-129629, from 11-133536 to 11-133539, 11-133542, 11-133543, 11-223898, 11-352627, 11-305377, 11-305378, 11-305384, 11-305380, 11-316435, 11-327076, 11-338096, 11-338098, 11-338099, and 11-343420, Japanese Patent Application Nos. 2000-187298,

2000-10229, 2000-47345, 2000-206642, 2000-98530, 2000-98531,  
2000-112059, 2000-112060, 2000-112104, 2000-112064, and  
2000-171936.

[0445]

### 15) Color Image Formation

Constitution of a multi-color photothermographic material may comprise a combination of at least two layers of different colors or may comprise one layer containing all colors therein as described in USP No. 4,708,928.

In a case of the multi-color photothermographic material, respective emulsion layers are, as described in USP No. 4,460,681, ordinarily maintained in a separate manner from one another by being provided with a functional or non-functional barrier layer between any two of the respective photosensitive layers.

[0446]

### 3. Image Forming Method

#### 3-1. Exposure

The photosensitive material according to the invention may be exposed by any method; however, it is preferable to use laser light as an exposure source. The silver halide emulsion having a high silver iodide content according to the invention has so far had a problem in that sensitivity thereof is low. However, it was found that the problem of such low sensitivity

is solved by performing writing-in by means of such an intense irradiation as laser light and image recording can be performed by a smaller energy than conventional. Thus, aimed sensitivity can be attained by performing writing-in by strong light in a short period of time.

[0447]

Particularly when a quantity of exposure which realizes a maximum density ( $D_{\max}$ ) is provided, a quantity of light on a surface of the photosensitive material is preferably in a range from  $0.1 \text{ W/mm}^2$  to  $100 \text{ W/mm}^2$ , more preferably from  $0.5 \text{ W/mm}^2$  to  $50 \text{ W/mm}^2$ , and most preferably from  $1 \text{ W/mm}^2$  to  $50 \text{ W/mm}^2$ .

[0448]

As for laser light according to the invention, a gas laser ( $\text{Ar}^+$ , He-Ne, or He-Cd), a YAG laser, a dye laser, a semiconductor laser and the like are preferable. Further, a combination of the semiconductor laser with a second harmonic generating element or the like can also be used. Preferable laser is, although being determined in correspondence to a light-absorbing peak wavelength of a spectral sensitizing dye or the like of the photothermographic material, He-Ne laser or red semiconductor laser which radiates red to infrared light, or  $\text{Ar}^+$ , He-Ne, or He-Cd laser, or blue semiconductor laser which radiates blue to green light. In recent years, particularly,

a module fabricated by unifying SHG (Second Harmonic Generator) element with the semiconductor laser, or the blue semiconductor laser has been developed, thereby rapidly attracting people's attention to a laser output device in a short wavelength region. Since the blue semiconductor laser is capable of performing ultra-fine image recording, increasing a recording density and obtaining a long-life and consistent output, it is expected that demand for the blue semiconductor laser will be increased. The peak wavelength of the laser light is, in terms of blue color, in a range from 300 nm to 500 nm and preferably from 400 nm to 500 nm, whereas, in terms of red to infrared, in a range from 600 nm to 900 nm and preferably from 620 nm to 850 nm.

[0449]

The laser light is favorably used in a manner in which it is oscillated in a vertical multi-mode by a method such as a high frequency superimposition method.

[0450]

### 3-2. Thermal Development

The photothermographic material according to the invention may be developed by any method. Ordinarily, a temperature of the photothermographic material which has imagewise been exposed is elevated to allow the

photothermographic material to be developed. A development temperature is preferably in a range from 80°C to 250°C, and more preferably from 100°C to 140°C.

A development time is preferably in a range from 1 second to 60 seconds, more preferably from 5 seconds to 30 seconds, and particularly preferably from 5 seconds to 20 seconds.

[0451]

A plate heater system is preferably used as a thermal development process. As for the thermal development process utilizing the plate heater system, processes as described in JP-A No. 11-133572 are preferable. These processes use a thermal development apparatus for obtaining a visible image by allowing the photothermographic material, in which a latent image has been formed, to contact a heating unit in a thermal development part. The heating unit comprises a plate heater and a plurality of pressing rollers arranged along one surface of the plate heater such that they face the surface. The photothermographic material is allowed to pass through between the pressing rollers and the plate heater to be thermally developed. It is preferable that the plate heater is divided into 2 to 6 steps, and that the top step has a temperature lowered by approximately 1°C to 10°C.

[0452]

Such methods are also described in JP-A No. 54-30032. According to these methods, moisture and organic solvents contained in the photothermographic material can be removed out of a system, and deformation of the support of the photothermographic material caused by rapid heating can also be suppressed.

[0453]

### 3-3. System

As for laser imagers each having an exposure part and a thermal development part for the medical diagnosis use, Fuji Medical Dry Imager FM-DP L and Fuji Medical Dry Imager DRYPIX 7000 (both manufactured by Fuji Photo Film Co., Ltd.) can be mentioned. Such systems are described in Fuji Medical Review No. 8, pp. 39 to 55 and techniques described therein can be utilized. Further, the photothermographic material according to the invention can also be applied as a photothermographic material for the laser imager in "AD network" proposed by Fuji Film Medical Systems as a network system adapted to DICOM Standards.

[0454]

### 4. Application of the Invention

The photothermographic material using a high silver iodide photographic emulsion according to the invention forms

a black-and-white image based on a silver image; hence, it is preferred that the photothermographic material is used as a photothermographic material for medical diagnosis, as a photothermographic material for industrial photography, as a photothermographic material for printing use, and as a photothermographic material for COM use.

[0455]

[Examples]

Hereinafter, specific examples are given below to illustrate the invention and should not be interpreted as limiting it in any way.

[0456]

Example 1

1. Preparation of PET Support and Undercoating

1-1. Film Forming

[0457]

PET having an intrinsic viscosity  $IV=0.66$  (measured at  $25^{\circ}\text{C}$  in phenol/tetrachlorethane=6/4 (ratio by weight)) was obtained in accordance with an ordinary preparation method by using terephthalic acid and ethylene glycol. After the thus-obtained PET is pelletized, the resultant pellets were dried at  $130^{\circ}\text{C}$  for 4 hours. Then, the thus-dried pellets was



extruded from a T-type die, and rapidly quenched, thereby preparing an unstretched film having a film thickness of 175  $\mu\text{m}$  after thermal fixation.

[0458]

The thus-prepared film was stretched up to 3.3 times in the machine direction with rollers having different peripheral velocities, then up to 4.5 times in the transverse direction by means of a tenter. The temperatures at the time of such stretching were 110°C and 130°C in the above sequence. Subsequently, the thus-stretched film was subjected to thermal fixation at 240°C for 20 seconds and, then, to relaxation by 4% in the transverse direction at the same temperature as at the thermal fixation. Thereafter, chucking parts of the tenter were slit off, and both edges of the film were subjected to knurl processing. The film was rolled at 4 kg/cm<sup>2</sup> to obtain a roll of film having a thickness of 175  $\mu\text{m}$ .

[0459]

#### 1-2. Corona Discharge Surface Treatment

Both surfaces of the support were treated at room temperature at the web handling velocity of 20 m/min by using a solid-state corona discharge processor Model 6KVA manufactured by Pillar Co. From values of electric current and voltage read at that time, it was found that a treatment

of 0.375 kV·A·min/m<sup>2</sup> was applied to the support. A treatment frequency was 9.6 kHz and a gap clearance between an electrode and a dielectric roll was 1.6 mm.

[0460]

### 1-3. Undercoat

#### 1) Preparation of Coating Solution for Undercoat Layer

Prescription-1 (For Undercoat Layer on Photosensitive Layer Side)

Pesresin A-520 (30% by mass solution) manufactured by Takamatsu Oil & Fat, Inc.	59 g
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Polyethylene glycol monononylphenyl ether (average number of ethylene oxide=8.5; 10% by mass solution)	5.4 g
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MP-1000 (polymeric fine grains; average grain diameter: 0.4 μm) manufactured by Soken Kagaku Co., Ltd.	0.91 g
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Distilled water	935 ml
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[0461]

Prescription-2 (For First Layer on Back Surface)

Styrene/butadiene copolymer latex (solid content: 40% by mass; weight ratio of styrene/butadiene=68/32)	158 g
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Sodium salt of 2,4-dichloro-6-hydroxy-S-triazine (8% by mass aqueous solution)	20 g
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Sodium laurylbenzene sulfonate (1% by mass aqueous solution)	10 ml
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Distilled water 854 ml

[0462]

Prescription-3 (For Second Layer on Back Surface)

SnO <sub>2</sub> /SbO (9/1 mass ratio; average grain diameter: 0.038 μm; 17% by mass dispersion)	84 g
Gelatin (10% by mass aqueous solution)	89.2 g
Metolose TC-5 (2% by mass aqueous solution) manufactured by Shin-Etsu Chemical Co., Ltd.	8.6 g
MP-1000 manufactured by Soken Kagaku Co., Ltd.	0.01 g
Sodium dodecylbenzene sulfonate (1% by mass aqueous solution)	10 ml
NaOH (1% by mass)	6 ml
Proxel manufactured by ICI Co., Ltd.	1 ml
Distilled water	805 ml

[0463]

2) Undercoating

After the corona discharge treatment was performed on both surfaces of a biaxially stretched polyethylene terephthalate support having a thickness of 175 μm, the undercoating solution of Prescription-1 was applied on one surface (photosensitive layer surface) thereof by means of a wire-bar in a wet coated quantity of 6.6 ml/m<sup>2</sup> (per one surface) and dried at 180°C for 5 minutes. Then, the undercoating

solution of Prescription-2 was applied on the opposite surface (back surface) by means of a wire-bar in a wet coated quantity of  $5.7 \text{ ml/m}^2$  and dried at  $180^\circ\text{C}$  for 5 minutes. Further, the undercoating solution of Prescription-3 was applied on the opposite surface (back surface) by means of a wire-bar in a wet coated quantity of  $7.7 \text{ ml/m}^2$  and dried at  $180^\circ\text{C}$  for 6 minutes to prepare an undercoated support.

[0464]

## 2. Preparation of Coating Material

### 1) Silver Halide Emulsion

#### (Preparation of Silver Halide Emulsion A)

To 1,421 ml of distilled water, 3.1 ml of a 1% by mass potassium bromide solution was added and, further, 3.5 ml of sulfuric acid having a concentration of 0.5 mol/L and 31.7 g of phthalated gelatin were added. While being kept stirring at  $30^\circ\text{C}$  in a reaction vessel made of stainless steel, the resultant mixture was added with an entire quantity of both of a solution A which has been prepared by adding distilled water to 22.22 g of silver nitrate to make an entire volume up to 95.4 ml and a solution B which has been prepared by adding distilled water to 15.3 g of potassium bromide and 0.8 g of potassium iodide to make an entire volume up to 97.4 ml at a constant flow-rate consuming 45 seconds and, then, added with 10 ml of a 3.5% by mass aqueous solution of hydrogen peroxide and, thereafter,

added with 10.8 ml of a 10% by mass aqueous solution of benzimidazole and, further, added with both of a solution C which has been prepared by adding distilled water to 51.86 g of silver nitrate to make an entire volume up to 317.5 ml and a solution D which has been prepared by adding distilled water to 44.2 g of potassium bromide and 2.2 g of potassium iodide to make an entire volume up to 400 ml such that an entire quantity of the solution C was added at a constant flow rate consuming 20 minutes and the solution D was added by a controlled-double-jet method while keeping a pAg value at 8.1 and, 10 minutes after such additions of the solution C and the solution D were started, added with an entire quantity of potassium hexachloroiridate (III) so as to be  $1 \times 10^{-4}$  mol, based on 1 mol of silver and, five seconds after the addition of the solution C was completed, added with an entire quantity of  $3 \times 10^{-4}$  mol, based on 1 mol of silver, of an aqueous solution of potassium hexacyanoiron (II). A pH of the resultant mixture was adjusted to 3.8 by using sulfuric acid having a concentration of 0.5 mol/L and, then, a stirring operation was stopped to perform precipitation/desalination/washing steps. Subsequently, a pH of the mixture thus subjected to these steps was adjusted to 5.9 by using sodium hydroxide having a concentration of 1 mol/L, thereby preparing a silver halide dispersion having a pAg value of 8.0.

[0465]

While being kept stirring at 38°C, the thus-prepared silver halide dispersion was added with 5 ml of a 0.34% by mass methanol solution of 1,2-benzisothiazolin-3-one and, after 40 minutes elapsed, heated to 47°C and, 20 minutes after such heating, added with  $7.6 \times 10^{-5}$  mol, based on 1 mol of silver, of a methanol solution of sodium benzene thiosulfonate and, after 5 minutes elapsed, added with  $2.9 \times 10^{-4}$  mol, based on 1 mol of silver, of a methanol solution of a tellurium sensitizing agent C and, then, ripened for 91 minutes and, thereafter, added with  $1.2 \times 10^{-3}$  mol, as a total of a spectral sensitizing dye A and a sensitizing dye B based on 1 mol of silver, of a methanol solution of a 3:1 mixture in a molar ratio of the spectral sensitizing dye A and the sensitizing dye B and, after one minute elapsed, added with 1.3 ml of a 0.8% by mass methanol solution of N,N'-dihydroxy-N''-diethylmelamine and, after 4 minutes elapsed, added with  $4.8 \times 10^{-3}$  mol, based on 1 mol of silver, of a methanol solution of 5-methyl-2-mercaptobenzimidazole,  $5.4 \times 10^{-3}$  mol, based on 1 mol of silver, of a methanol solution of 1-phenyl-2-heptyl-5-mercapto-1,3,4-triazole, and  $8.5 \times 10^{-3}$  mol, based on 1 mol of silver, of an aqueous solution of a 1-(3-methylureidophenyl)-5-mercaptotetrazole, thereby preparing a silver halide emulsion 1A.

[0466]

Grains in the thus-prepared silver halide emulsion were silver iodobromide grains in cubic form having (100) face ratio of 80%, an average sphere-equivalent diameter of 0.042  $\mu\text{m}$ , a variation coefficient of a sphere-equivalent diameter of 20%, and uniformly containing 3.5 mol% of iodine. A grain size or the like was determined based on an average of 1,000 grains obtained by using an electron microscope.

[0467]

(Preparation of Silver Halide Emulsion B)

A silver halide emulsion B was prepared in a same manner as in the preparation of the silver halide emulsion A except for removing potassium iodide. Grains in the thus-prepared silver halide emulsion were silver bromide grains in cubic form having (100) face ratio of 85%, an average sphere-equivalent diameter of 0.07  $\mu\text{m}$ , and a variation coefficient of a sphere-equivalent diameter of 15%.

[0468]

(Preparation of Silver Halide Emulsion C)

To 1,420 ml of distilled water, 4.3 ml of a 1% by mass potassium iodide solution was added and, further, 3.5 ml of sulfuric acid having a concentration of 0.5 mol/L and 36.7 g of phthalated gelatin were added. While being kept stirring at 35°C in a reaction vessel made of stainless steel, the resultant

mixture was added with an entire quantity of both of a solution A which has been prepared by adding distilled water to 22.22 g of silver nitrate to make an entire volume up to 195.6 ml and a solution B which has been prepared by adding distilled water to 21.8 g of potassium iodide to make an entire volume up to 219 ml at a constant flow-rate consuming 9 minutes and, then, added with 10 ml of a 3.5% by mass aqueous solution of hydrogen peroxide and, thereafter, added with 10.8 ml of a 10% by mass aqueous solution of benzimidazole and, further, added with both of a solution C which has been prepared by adding distilled water to 51.86 g of silver nitrate to make an entire volume up to 317.5 ml and a solution D which has been prepared by adding distilled water to 60 g of potassium iodide to make an entire volume up to 600 ml such that an entire quantity of the solution C was added at a constant flow rate consuming 120 minutes and the solution D was added by a controlled-double-jet method while keeping a pAg value at 8.1.

[0469]

10 minutes after such additions of the solution C and the solution D were started, added with an entire quantity of potassium hexachloroiridate (III) so as to be  $1 \times 10^{-4}$  mol, based on 1 mol of silver and, five seconds after the addition of the solution C was completed, added with an entire quantity of  $3 \times 10^{-4}$  mol, based on 1 mol of silver, of an aqueous solution of potassium



hexacyanoiron (II). A pH of the resultant mixture was adjusted to 3.8 by using sulfuric acid having a concentration of 0.5 mol/L and, then, a stirring operation was stopped to perform precipitation/desalination/washing steps. Subsequently, a pH of the mixture thus subjected to these steps was adjusted to 5.9 by using sodium hydroxide having a concentration of 1 mol/L, thereby preparing a silver halide dispersion having a pAg value of 8.0.

[0470]

While being kept stirring at 38°C, the thus-prepared silver halide dispersion was added with 5 ml of a 0.34% by mass methanol solution of 1,2-benzisothiazolin-3-one and, then, heated to 47°C and, 20 minutes after such heating, added with  $7.6 \times 10^{-5}$  mol, based on 1 mol of silver, of a methanol solution of sodium benzene thiosulfonate and, after 5 minutes elapsed, added with  $2.9 \times 10^{-4}$  mol, based on 1 mol of silver, of a methanol solution of a tellurium sensitizing agent C and, then, ripened for 91 minutes and, thereafter, added with 1.3 ml of a 0.8% by mass methanol solution of N,N'-dihydroxy-N''-diethylmelamine and, after 4 minutes elapsed, added with  $4.8 \times 10^{-3}$  mol, based on 1 mol of silver, of a methanol solution of 5-methyl-2-mercaptobenzimidazole, and  $5.4 \times 10^{-3}$  mol, based on 1 mol of silver, of a methanol solution of 1-phenyl-2-heptyl-5-mercapto-1,3,4-triazole, thereby

preparing a silver halide emulsion C.

[0471]

The grain in the thus-prepared silver halide emulsion was in tetradecahedral form having (100), {100}, and {101} faces and a ratio of  $\gamma$  phase thereof was 30%. Further, the grain was a pure silver iodide grain having an average sphere-equivalent diameter of 0.30  $\mu\text{m}$  and a variation coefficient of a sphere-equivalent diameter of 15%. A size or the like of the grain was determined based on an average of 1000 grains obtained by using an electron microscope.

[0472]

(Preparation of Silver Halide Emulsion D)

To 1,421 ml of distilled water, 4.3 ml of a 1% by mass potassium iodide solution was added and, further, 3.5 ml of sulfuric acid having a concentration of 0.5 mol/L, 36.5 g of phthalated gelatin, and 160 ml of a 5% by mass methanol solution of 2,2'-(ethylenedithio)diethanol were added. While being kept stirring at 75°C in a reaction vessel made of stainless steel, the resultant mixture was added with both of a solution A which has been prepared by adding distilled water to 22.22 g of silver nitrate to make an entire volume up to 218 ml and a solution B which has been prepared by adding distilled water to 36.6 g of potassium iodide to make an entire volume up to

366 ml such that an entire quantity of the solution A was added at a constant flow-rate consuming 38 minutes and the solution B was added by a controlled-double-jet method while keeping a pAg value at 10.2 and, then, added with 10 ml of a 3.5% by mass aqueous solution of hydrogen peroxide and, thereafter, added with 10.8 ml of a 10% by mass aqueous solution of benzimidazole and, further, added with both of a solution C which has been prepared by adding distilled water to 51.86 g of silver nitrate to make an entire volume up to 508.2 ml and a solution D which has been prepared by adding distilled water to 63.9 g of potassium iodide to make an entire volume up to 639 ml such that an entire quantity of the solution C was added at a constant flow rate consuming 63 minutes and the solution D was added by a controlled-double-jet method while keeping a pAg value at 10.2. Then, 10 minutes after such additions of the solution C and the solution D were started, the resultant mixture was added with an entire quantity of potassium hexachloroiridate (III) so as to be  $1 \times 10^{-4}$  mol, based on 1 mol of silver and, five seconds after the addition of the solution C was completed, added with an entire quantity of  $3 \times 10^{-4}$  mol, based on 1 mol of silver, of an aqueous solution of potassium hexacyanoiron (II). A pH of the resultant mixture was adjusted to 3.8 by using sulfuric acid having a concentration of 0.5 mol/L and, then, a stirring operation was stopped to perform precipitation/desalination/washing steps. Subsequently, a pH

of the mixture thus subjected to these steps was adjusted to 5.9 by using sodium hydroxide having a concentration of 1 mol/L, thereby preparing a silver halide dispersion having a pAg value of 11.0.

[0473]

While being kept stirring at 38°C, the thus-prepared silver halide dispersion was added with 5 ml of a 0.34% by mass methanol solution of 1,2-benzisothiazolin-3-one and, after 40 minutes elapsed, heated to 47°C and, 20 minutes after such heating, added with  $7.6 \times 10^{-5}$  mol, based on 1 mol of silver, of a methanol solution of sodium benzene thiosulfonate and, after 5 minutes elapsed, added with  $2.9 \times 10^{-4}$  mol, based on 1 mol of silver, of a methanol solution of a tellurium sensitizing agent C and, then, ripened for 91 minutes and, thereafter, added with  $1.2 \times 10^{-3}$  mol, as a total of sensitizing dyes A and B based on 1 mol of silver, of a methanol solution of a 3:1 mixture in a molar ratio of the sensitizing dyes A and B and, after one minute elapsed, added with 1.3 ml of a 0.8% by mass methanol solution of N,N'-dihydroxy-N"-diethylmelamine and, after 4 minutes elapsed, added with  $4.8 \times 10^{-3}$  mol, based on 1 mol of silver, of a methanol solution of 5-methyl-2-mercaptobenzimidazole,  $5.4 \times 10^{-3}$  mol, based on 1 mol of silver, of a methanol solution of 1-phenyl-2-heptyl-5-mercapto-1,3,4-triazole, and  $8.5 \times 10^{-3}$  mol, based on 1 mol of silver, of an aqueous solution of a

1-(3-methylureidophenyl)-5-mercaptotetrazole, thereby preparing a silver halide emulsion D.

[0474]

The thus-prepared silver halide emulsion D was a pure silver iodide emulsion in which tabular grains having an average projected area diameter of 1.369  $\mu\text{m}$ , a variation coefficient of the average projected area diameter of 19.7%, an average thickness of 0.130  $\mu\text{m}$ , and an average aspect ratio of 11:1 occupy 80% or more of an entire projected area. A sphere-equivalent diameter of the grain was 0.707  $\mu\text{m}$ . As a result of an X-ray powder diffraction analysis, it was found that 90% or more of silver iodide was present in a form of  $\gamma$  phase.

An electron micrograph of the grains of the silver halide emulsion D is shown in Fig. 1. The electron micrograph was taken at a shadowing angle of 15 degrees. Spherical grains in Fig. 1 show grains of latex used as reference. Such grain of latex has a size of 0.5  $\mu\text{m}$ .

[0475]

(Preparation of Silver Halide Emulsions E and F)

A silver halide emulsions 1E and 1F, as shown in Fig. 1, were prepared in a same manner as in the preparation of the silver halide emulsion D except for appropriately changing a quantity of a 5% by mass methanol solution of

2,2'-(ethylenedithio)diethanol to be added, a temperature at the time of grain-forming, and an adding time of the solution A.

[0476]

[Table 1]

	Average projected area diameter ( $\mu\text{m}$ )	Variation coefficient of Average projected area (%)	Average grain thickness ( $\mu\text{m}$ )	Average aspect ratio	Average sphere equivalent diameter ( $\mu\text{m}$ )
Emulsion D	1.369	19.7	0.130	11.1	0.707
Emulsion E	1.140	19.7	0.112	10.6	0.592
Emulsion F	0.907	20.3	0.107	9.0	0.417

[0477]

## 2) Preparation of Fatty Acid Silver Salt Dispersion A

### <Preparation of Recrystallized Behenic Acid>

100 kg of behenic acid (product name: Edenor C22-85R; manufactured by Henkel Co.) was added to 1200 kg of isopropyl alcohol, dissolved therein at 50°C, filtered by a filter of 10  $\mu\text{m}$ , and cooled to 30°C to be recrystallized. A cooling speed at the time of such recrystallization was controlled to be 3°C/hour. Such crystal obtained in a manner as described above was subjected to centrifugal filtration, rinsed with 100 kg of isopropyl alcohol by sprinkling, and dried. The thus-dried

crystal was esterified and subjected to a GC-FID measurement to find that the crystal contained 96 mol% of behenic acid, 2 mol% of lignoceric acid, 2 mol% of arachidic acid, and 0.001 mol% of erucic acid.

[0478]

<Preparation of Fatty Acid Silver Salt Dispersion>

88 kg of recrystallized behenic acid, 422 L of distilled water, 49.2 L of an aqueous solution of NaOH having a concentration of 5 mol/L and 120 L of t-butyl alcohol were mixed and, then, while being kept stirring at 75°C for 1 hour, allowed to react with one another to obtain a sodium behenate solution B. Apart from the sodium behenate solution B, 206.2 L of an aqueous solution (pH: 4.0) containing 40.4 kg of silver nitrate was prepared and maintained at 10°C. A reaction vessel charged with 635 L of distilled water and 30 L of t-butyl alcohol was maintained at 30°C and, then, while being kept sufficiently stirring, charged with an entire quantity of the foregoing sodium behenate solution B and an entire quantity of the foregoing silver nitrate aqueous solution at a constant flow rate consuming 93 minutes 15 seconds and 90 minutes, respectively. At that time, the silver nitrate aqueous solution was solely added for 11 minutes after the addition of the silver nitrate aqueous solution was started. After that, the addition of the sodium behenate solution was started. For 14 minutes 15 seconds after

the addition of the silver nitrate aqueous solution was completed, the sodium behenate solution was solely added. At that time, a temperature inside the reaction vessel was maintained at 30°C and a solution temperature was maintained constant by means of an external temperature control. Further, piping of an addition system for the sodium behenate solution was warmed by circulating warm water in an outer part of a double-walled tube so that the solution temperature at an outlet of an addition nozzle tip was adjusted to be 75°C. Piping of an addition system of the aqueous silver nitrate solution was also heat-controlled by circulating cold water in an outer part of a double-walled tube. Positions where the sodium behenate solution and the aqueous silver nitrate solution were added were arranged symmetrically in relation to a stirring shaft in the center, and respective heights of the positions were adjusted such that they do not touch a reaction solution.

[0479]

After the addition of the sodium behenate solution was completed, the resultant reaction solution was held at a temperature thereof as it was for 20 minutes with stirring and, then, the temperature was elevated up to 35°C consuming 30 minutes. After that, the reaction solution was ripened for 210 minutes. Immediately after such ripening, the solid content was separated by centrifugal filtration and, then, the thus-separated solid



content was rinsed with water until electrical conductivity of the filtrate reached 30  $\mu\text{S}/\text{cm}$ . Thus, a fatty acid silver salt was obtained. A solid substance obtained in such a manner as described above was stored as a wet cake without drying.

[0480]

Shapes of silver behenate grains thus obtained were evaluated by electron microscopic photography. The obtained silver behenate grains were crystals having average values of  $a=0.21\ \mu\text{m}$ ,  $b=0.4\ \mu\text{m}$  and  $c=0.4\ \mu\text{m}$ , an average aspect ratio of 2.1, and a variation coefficient of a sphere-equivalent diameter of 11% ( $a$ ,  $b$  and  $c$  were defined according to respective definitions previously described herein).

[0481]

19.3 kg of polyvinyl alcohol (trade name: PVA-217; manufactured by Kuraray Co., Ltd.) and water were added to the thus-stored wet cake corresponding to 260 kg of dried solid content to make an entire quantity of the resultant mixture up to 1,000 kg and, then, the resultant mixture was changed into a slurry by means of dissolver-blades. Further, the slurry was preliminarily dispersed with a pipeline-mixer (Model PM-10; manufactured by Mizuho Industrial Co., Ltd.)

[0482]

Then, the thus-preliminarily-dispersed starting solution was processed three times with a dispersing machine (trade name: Microfluidizer M-610 equipped with a Z-type interaction chamber; manufactured by Microfluidex International Corporation) under a pressure adjusted to 1,150 kg/cm<sup>2</sup> to obtain a silver behenate dispersion. A dispersion temperature was set at 18°C by adjusting a temperature of coolant such that a cooling operation was performed by using coil type heat exchangers installed in front and rear of the interaction chamber, respectively.

[0483]

### 3) Preparation of Reduction agent Dispersion

#### (Preparation of Reduction agent-1 Dispersion)

10 kg of water was added to 10 kg of a reduction agent-1 (2,2'-methylene-bis(4-ethyl-6-tert-butyl phenol) and 16 kg of a 10% by mass aqueous solution of modified polyvinylalcohol (POVAL MP203 manufactured by Kuraray Co. Ltd.). The resultant mixture was thoroughly mixed to form a slurry. The slurry was fed by means of a diaphragm pump into a horizontal-type sand mill (UVM-2 manufactured by Imex Co., Ltd.) filled with zirconia beads having an average diameter of 0.5 mm, and dispersed therein for 3 hours. Then, 0.2 g of a sodium salt of benzisothiazolinone and water were added to the resultant dispersion so as to allow a concentration of the reduction agent to be 25% by mass. The

resultant dispersion was heated at 60°C for 5 hours, thereby obtaining a reduction agent-1 dispersion. Reduction agent grains contained in the thus-obtained reduction agent dispersion had a median diameter of 0.40  $\mu\text{m}$  and a maximum grain diameter of 1.4  $\mu\text{m}$  or less. The reduction agent dispersion was filtrated with a filter made of polypropylene having a pore diameter of 3.0  $\mu\text{m}$  to remove foreign matters such as dust and, then, stored.

[0484]

(Preparation of Reduction agent-2 Dispersion)

10 kg of water was added to 10 kg of a reduction agent-2 (6,6'-di-t-butyl-4,4'-dimethyl-2,2'-butylidene diphenol), and 16 kg of a 10% by mass aqueous solution of modified polyvinylalcohol (POVAL MP203 manufactured by Kuraray Co. Ltd.). The resultant mixture was thoroughly mixed to form a slurry. The slurry was fed by means of a diaphragm pump into a horizontal-type sandmill (UVM-2 manufactured by Imex Co., Ltd.) filled with zirconia beads having an average diameter of 0.5 mm, and dispersed for 3 hours 30 minutes. Then, 0.2 g of a sodium salt of benzisothiazolinone and water were added to the resultant dispersion so as to allow a concentration of the reduction agent to be 25% by mass. The resultant dispersion was heated at 40°C for one hour and, subsequently, at 80°C for one hour to obtain a reduction agent-2 dispersion. Reduction agent grains

contained in the thus-obtained reduction agent dispersion had a median diameter of 0.50  $\mu\text{m}$  and a maximum grain diameter of 1.6  $\mu\text{m}$  or less. The reduction agent dispersion was filtrated with a filter made of polypropylene having a pore diameter of 3.0  $\mu\text{m}$  to remove foreign matters such as dust and, then, stored.

[0485]

#### 4) Preparation of Hydrogen Bonding-Type Compound-1 Dispersion

10 kg of water was added to 10 kg of a hydrogen bonding-type compound-1 (tri(4-t-butylphenyl)phosphine oxide), and 16 kg of a 10% by mass aqueous solution of modified polyvinylalcohol (POVAL MP203 manufactured by Kuraray Co., Ltd.). The resultant mixture was thoroughly mixed to form a slurry. The slurry was fed by means of a diaphragm pump into a horizontal-type sand mill (UVM-2 manufactured by Imex Co., Ltd.) filled with zirconia beads having an average diameter of 0.5 mm, and dispersed for 4 hours. Then, 0.2 g of a sodium salt of benzisothiazolinone and water were added to the resultant dispersion so as to allow a concentration of the hydrogen bonding-type compound to be 25% by mass. The resultant dispersion was heated at 40°C for one hour and, subsequently, at 80°C for one hour, thereby obtaining a hydrogen bonding-type compound-1 dispersion. Hydrogen bonding-type compound grains contained in the thus-obtained hydrogen bonding-type compound dispersion had a median diameter of 0.45  $\mu\text{m}$  and a maximum grain diameter of

1.3  $\mu\text{m}$  or less. The hydrogen bonding-type compound dispersion was filtrated with a filter made of polypropylene having a pore diameter of 3.0  $\mu\text{m}$  to remove foreign matters such as dust and, then, stored.

[0486]

#### 5) Preparation of Development Accelerator-1 Dispersion

10 kg of water was added to 10 kg of a development accelerator-1, and 20 kg of a 10% by mass aqueous solution of modified polyvinylalcohol (POVAL MP203 manufactured by Kuraray Co., Ltd.). The resultant mixture was thoroughly mixed to form a slurry. The slurry was fed by means of a diaphragm pump into a horizontal-type sand mill (UVM-2 manufactured by Imex Co., Ltd.) filled with zirconia beads having an average diameter of 0.5 mm, and dispersed for 3 hours 30 minutes. Then, 0.2 g of a sodium salt of benzisothiazolinone and water were added to the resultant dispersion so as to allow a concentration of the development accelerator to be 20% by mass, thereby obtaining a development accelerator-1 dispersion. Development accelerator grains contained in the thus-obtained development accelerator dispersion had a median diameter of 0.48  $\mu\text{m}$  and a maximum grain diameter of 1.4  $\mu\text{m}$  or less. The development accelerator dispersion was filtrated with a filter made of polypropylene having a pore diameter of 3.0  $\mu\text{m}$  to remove foreign matters such as dust and, then, stored.

Solid dispersions of a development accelerator-2 and a color tone adjusting agent-1 were dispersed in a same manner as in the development accelerator-1, thereby obtaining 20% by mass and 15% by mass dispersions, respectively.

[0487]

#### 6) Preparation of Organic Polyhalogen Compound Dispersion

(Preparation of Organic Polyhalogen Compound Dispersion a)

14 kg of water was added to 10 kg of an organic polyhalogen compound-1, 10 kg of a 20% by mass aqueous solution of modified polyvinylalcohol (trade name: POVAL MP203), and 0.4 kg of a 20% by mass aqueous solution of sodium triisopropyl naphthalene sulfonate. The resultant mixture was thoroughly mixed to form a slurry. The slurry was fed by means of a diaphragm pump into a horizontal-type sand mill (trade name: UVM-2) filled with zirconia beads having an average diameter of 0.5 mm, and dispersed for 5 hours. Then, 0.2 g of a sodium salt of benzisothiazolinone and water were added to the resultant dispersion so as to allow a concentration of the organic polyhalogen compound to be 26% by mass, thereby obtaining an organic polyhalogen compound dispersion (a). Organic polyhalogen compound grains contained in the thus-obtained organic polyhalogen compound dispersion had a median diameter of 0.41  $\mu\text{m}$  and a maximum grain diameter of 2.0  $\mu\text{m}$  or less. The organic polyhalogen compound dispersion was filtrated with a

filter made of polypropylene having a pore diameter of 10.0  $\mu\text{m}$  to remove foreign matters such as dust and, then, stored.

[0488]

(Preparation of Organic Polyhalogen Compound Dispersion b)

8 kg of water was added to 10 kg of an organic polyhalogen compound-2, 20 kg of a 10% by mass aqueous solution of modified polyvinylalcohol (trade name: POVAL MP203), and 0.4 kg of a 20% by mass aqueous solution of sodium triisopropyl naphthalene sulfonate. The resultant mixture was thoroughly mixed to form a slurry. The slurry was fed by means of a diaphragm pump into a horizontal-type sand mill (trade name: UVM-2) filled with zirconia beads having an average diameter of 0.5 mm, and dispersed for 5 hours. Then, 0.2 g of a sodium salt of benzisothiazolinone and water were added to the resultant dispersion so as to allow a concentration of the organic polyhalogen compound to be 25% by mass. The resultant dispersion was heated at 40°C for 5 hours, thereby obtaining an organic polyhalogen compound dispersion. Organic polyhalogen compound grains contained in the thus-obtained organic polyhalogen compound dispersion had a median diameter of 0.36  $\mu\text{m}$  and a maximum grain diameter of 1.5  $\mu\text{m}$  or less. The organic polyhalogen compound dispersion was filtrated with a filter made of polypropylene having a pore diameter of 3.0  $\mu\text{m}$  to remove foreign matters such as dust and, then, stored.

[0489]

7) Preparation of Silver Iodide Complex Forming Agent

(Compound No. F-440)

8 kg of modified polyvinyl alcohol (trade name: MP203) was dissolved in 174.57 kg of water. Then, 3.15 kg of a 20% by mass aqueous solution of sodium triisopropyl naphthalene sulfonate and 14.28 kg of a 70% by mass aqueous solution of the compound No. F-440 to the resultant mixture, thereby preparing a 5% by mass solution of the compound No. F-440. (Preparation of Other Silver Iodide Complex Forming Agent Dispersions)

250 g of water was added to 64 g of a silver iodide complex forming agent shown in Table 1 and 6.4 g of DEMOL N (manufactured by Kao Corporation). The resultant mixture was thoroughly mixed to form a slurry. The slurry, together with 800 g of zirconia beads having an average diameter of 0.5 mm which have previously been prepared, was fed into a vessel and, then, dispersed for 8 hours by a dispersing device (1/4 G Sand-Grinder Mill: manufactured by Imex Co., Ltd.). The resultant dispersion was taken out of the vessel and, then, diluted with water, thereby obtaining a dispersion having a compound concentration of 5% by mass. Compound grains in the thus-obtained dispersion had an average grain diameter of 0.40  $\mu\text{m}$ .



[0490]

#### 8) Preparation of SBR Latex Liquid

An SBR latex at  $T_g = 23^\circ\text{C}$  was prepared in a manner as described below.

70.5 parts by mass of styrene, 26.5 parts by mass of butadiene, and 3 parts by mass of acrylic acid were allowed to be emulsify-polymerized thereamong by using ammonium persulfate as a polymerization initiator and an anionic surfactant as an emulsifying agent. The resultant reaction product was subjected to aging at  $80^\circ\text{C}$  for 8 hours and, then, cooled to be  $40^\circ\text{C}$  and, then, a pH thereof was adjusted to be 7.0 by using an aqueous ammonia solution. Further, the resultant mixture was added with SANDET BL (manufactured by Sanyo Chemical Industries, Ltd.) to allow a concentration thereof to be 0.22%. Next, a pH of the resultant mixture was adjusted to be 8.3 by using an aqueous 5% NaOH solution and, further, adjusted to be 8.4 by using an aqueous ammonia solution; on this occasion, a molar ratio of  $\text{Na}^+$  ion to  $\text{NH}_4^+$  ion which was employed was 1:2.3. Still further, 0.15 ml, based on 1 kg of the thus-pH-adjusted mixture, of an aqueous 7% solution of a sodium salt of benzisothiazolinone was added thereto, thereby preparing an SBR latex solution.

[0491]

(SBR latex: latex of -St(70.5)-Bu(26.5)-AA(3))

Properties of the latex were as follows: an average grain diameter at  $T_g=23^{\circ}\text{C}$ :  $0.1\ \mu\text{m}$ ; concentration: 43% by mass; equilibrium moisture content at  $25^{\circ}\text{C}$  60% RH: 0.6% by mass; ionic conductance:  $4.2\ \text{mS/cm}$  (as for ionic conductance, latex starting solution (43% by mass) was measured at  $25^{\circ}\text{C}$  by using a diaphragm (CM-30S manufactured by DKK-TOA Corporation); and pH: 8.4.

[0492]

#### 9) Preparation of Mercapto Compound

(Preparation of Aqueous Solution of Mercapto Compound-1)

7 g of a mercapto compound-1 (sodium salt of 1-(3-sulfophenyl)-5-mercaptotetrazole) was dissolved in 993 g of water to prepare a 0.7% by mass aqueous solution.

[0493]

(Preparation of Aqueous Solution of Mercapto Compound-2)

20 g of a mercapto compound-2 (1-(3-methylureidophenyl)-5-mercaptotetrazole) was dissolved in 980 g of water to prepare a 2.0% by mass aqueous solution.

[0494]

### 3. Preparation of Coating Solution

#### 1) Preparation of Image Forming Layer

1,000 g of the fatty acid silver salt dispersion A obtained

in a manner as described above, 220 ml of water, 6.3 g of the organic polyhalogen compound dispersion (a), 20.7 g of the organic polyhalogen compound dispersion (b), 1,082 g of an SBR latex (T<sub>g</sub>: 23°C) solution, 75 g of the reduction agent-1 dispersion, 75 g of the reduction agent-2 dispersion, 106 g of the hydrogen bonding-type compound-1 dispersion, 4.8 g of the development accelerator-1 dispersion, 9 ml of the mercapto compound-1 aqueous solution, and 27 ml of the mercapto compound-2 aqueous solution were mixed in the stated order to prepare a mixture. The thus-prepared mixture was, further, added with the silver iodide complex forming agent (shown in Table 1) and, immediately before coating, added with 0.25 mol in a silver quantity, based on 1 mol of the fatty acid silver salt, of the silver halide emulsion (shown in Table 1) and, then, thoroughly mixed. Thereafter, the resultant mixture was fed to a coating die as it was to be applied.

[0495]

## 2) Preparation of Coating Solution for Intermediate Layer

2 ml of a 5% by mass aqueous solution of Aerosol OT (manufactured by American Cyanamid Company) and 10.5 ml of a 20% by mass aqueous solution of diammonium phthalate were added to 772 g of a 10% by mass aqueous solution of polyvinyl alcohol (PVA-205 manufactured by Kuraray Co., Ltd.), 5.3 g of a pigment-1 dispersion, and 226 ml of a 27.5% by mass solution of a latex

of a methyl methacrylate/styrene/butyl acrylate/hydroxyethyl methacrylate/acrylic acid copolymer (copolymerization ratio by mass: 64/9/20/5/2) to prepare a mixture. Then, the thus-prepared mixture was added with water so as to make an entire quantity of the mixture up to 880 g. A pH value of the thus-made mixture was adjusted to be 7.5 by using NaOH, thereby obtaining a coating solution for an intermediate layer. The coating solution was fed to a coating die such that a coating quantity became 10 ml/m<sup>2</sup>.

Viscosity of the coating solution measured by a B-type viscometer (No. 1 rotor at 60 rpm) was 65 [mPa·s] at 40°C.

[0496]

### 3) Preparation of Coating Solution for First Layer of Surface Protective Layer

64 g of inert gelatin was dissolved in water. To the resultant gelatin solution, added were 80 g of a 27.5% by mass solution of a latex of a methyl methacrylate/styrene/butyl acrylate/hydroxyethyl methacrylate/acrylic acid copolymer (copolymerization ratio by mass: 64/9/20/5/2), 23 ml of a 10% by mass methanol solution of phthalic acid, 23 ml of a 10% by mass aqueous solution of 4-methyl phthalic acid, 28 ml of sulfuric acid having a concentration of 0.5 mol/L, 5 ml of a 5% by mass aqueous solution of Aerosol OT, 0.5 g of phenoxyethanol and 0.1 g of benzisothiazolinone to prepare a mixture. Then,

the thus-prepared mixture was added with water to make an entire quantity of the mixture up to be 750 g, thereby obtaining a coating solution. Immediately before coating, the coating solution was mixed with 26 ml of a 4% by mass chrome alum solution by using a static mixer and, then, fed to a coating die such that a coating quantity became 18.6 ml/m<sup>2</sup>.

Viscosity of the coating solution measured by a B-type viscometer (No. 1 rotor at 60 rpm) was 20 [mPa·s] at 40°C.

[0497]

#### 4) Preparation of Coating Solution for Second Layer of Surface Protective Layer

80 g of inert gelatin was dissolved in water. To the resultant gelatin solution, added were 102 g of a 27.5% by mass solution of a latex of a methyl methacrylate/styrene/butyl acrylate/hydroxyethyl methacrylate/acrylic acid copolymer (copolymerization ratio by mass: 64/9/20/5/2), 3.2 ml of a 5% by mass solution of a fluorine-type surfactant (F-1), 32 ml of a 2% by mass solution of a fluorine-type surfactant (F-2), 23 ml of a 5% by mass solution of Aerosol OT, 4 g of polymethyl methacrylate fine grains (average grain diameter: 0.7 μm), 21 g of polymethyl methacrylate fine grains (average grain diameter: 4.5 μm), 1.6 g of 4-methyl phthalic acid, 4.8 g of phthalic acid, 44 ml of sulfuric acid having a concentration of 0.5 mol/L, and 10 mg of benzisothiazolinone to prepare a

mixture. Then, the thus-prepared mixture was added with water to make an entire quantity of the mixture up to 650 g. Immediately before coating, the thus-made mixture was mixed with 445 ml of an aqueous solution containing 4% by mass of chrome alum and 0.67% by mass of phthalic acid by using a static mixer, thereby obtaining a coating solution for a second layer for a protection layer of an emulsion layer. The thus-obtained coating solution was, then, fed to a coating die such that a coating quantity became 8.3 ml/m<sup>2</sup>.

Viscosity of the coating solution measured by a B-type viscometer (No. 1 rotor at 60 rpm) was 19 [mPa·s] at 40°C.

[0498]

#### 4. Coating

The image-forming layer, the intermediate layer, the first layer for the surface protection layer, and the second layer for the surface protection layer were applied in the stated order in a simultaneous multi-layer manner. A coated silver quantity in the image-forming layer was 1.65 g/m<sup>2</sup> as a sum of the fatty acid silver salt and the silver halide.

[0499]

#### 5. Evaluation of Performance

##### 1) Preparation

Each of the thus-obtained samples was cut into pieces

of a half-size, wrapped with a wrapping material as mentioned below in an environment of 25°C 50% RH and, then, stored for 2 weeks at room temperature.

(Wrapping Material)

The wrapping material used was 50  $\mu\text{m}$  thick polyethylene film comprising PET: 10  $\mu\text{m}$ /PE: 12  $\mu\text{m}$ /aluminum foil: 9  $\mu\text{m}$ /Ny: 15  $\mu\text{m}$  /PE: 50  $\mu\text{m}$  containing 3% by mass of carbon. Oxygen transmittance was 0.02 ml/atm·m<sup>2</sup>·25°C·day; and moisture transmittance was 0.10 g/atm·m<sup>2</sup>·25°C·day.

[0500]

2) Evaluation Condition

(Measurement of Transmission Density of Film)

Ultraviolet visible region transmission densities before and after thermal development of unexposed samples were measured by making use of spectral absorption spectra.

Thermal development condition: samples were thermally developed by using a thermal development part of Fuji Medical Dry Laser Imager FM-DPL for 24 seconds in which temperatures of 4 panels of a 4-panel-type panel heater were set at 112°C, 119°C, 121°C and 121°C, respectively.

Measuring Device: a spectrophotometer (U-4100 manufactured by Hitachi, Ltd.)

Results of such measurement are shown in Fig. 2. In Fig. 2, a solid line indicates absorption spectra before the thermal

development while a broken line indicates absorption spectra after the thermal development.

[0501]

(Observation of Silver Halide Grain in Film by Electron Microscope)

An ultrathin section of a film of each of samples before and after the thermal development was photographed by a transmission electron microscope.

Photographing condition: each sample was shaved by a diamond cutter to prepare a thin section having a thickness of about 0.1  $\mu\text{m}$  which was, then, put on the observation.

In regard to sample No. 10, a photograph (A) showing that before the thermal development and a photograph (B) showing that after the thermal development are shown in Fig.3.

[0502]

### 3) Evaluation of Sample

Obtained results are shown in Table 2.

From Fig. 2, in regard to samples before the thermal development, a characteristic maximum absorption was noticed in the vicinity of 423 nm. The characteristic maximum absorption was effected by a transition absorption caused by a high silver iodide phase. Meanwhile, in regard to samples after the thermal development, the transition absorption was



reduced to be 1/2 or less of the former one or disappeared. Haze of the film was also disappeared, thereby forming a transparent film.

From Fig. 3, in regard to the sample A before the thermal development, a tabular cross-section was observed as in a rod-like shape derived from the fact that the tabular silver halide grains are aligned on a plane while in regard to the sample B after the thermal development, it is found that such grains were disappeared.

[0503]

[Table 2]

Sample No.	Silver halide emulsion		Silver iodide complex forming agent		Absorption spectral*	Electron microscopy of Ultrathin section**	Remarks
	Emulsion No.	Shape, size	Compound No.	Addition quantity			
1	A (AgBr3.5)	Cubic	-	-	No change	Remained	Comparative Example
2	ditto	ditto	F-440	8 mol%	No change	Remained	Comparative Example
3	B (AgBr)	ditto	-	-	No change	Remained	Comparative Example
4	C	ditto	F-440	8 mol%	No change	Remained	Comparative Example
5	ditto	Tetradecahedron	-	-	No change	Remained	Comparative Example
6	ditto	ditto	F-440	8 mol%	Disappeared	Disappeared	Prsesnt invention
7	ditto	ditto	F-431	ditto	Disappeared	Disappeared	Prsesnt invention
8	ditto	ditto	F-443	ditto	Disappeared	Disappeared	Prsesnt invention
9	ditto	ditto	F-444	ditto	Disappeared	Disappeared	Prsesnt invention
10	D	Tabular	F-440	ditto	Disappeared	Disappeared	Prsesnt invention
11	E	ditto	ditto	ditto	Disappeared	Disappeared	Prsesnt invention
12	F	ditto	ditto	ditto	Disappeared	Disappeared	Prsesnt invention

(Absorption spectral\*: Change of transition absorption)

(Electron microscopy of Ultrathin section\*\*: Observation of silver halide grain)

The quantity of the silver iodide complex forming agent to be coated is based on 1 mol of silver behenate.

[0504]

The transmission density of the film was reduced when it was thermally developed, by adding the silver iodide complex forming agent to the silver halide emulsion having a high iodine content according to the invention. As a result of the observation by a transmission electron microscope, in regard to samples according to the invention, the silver halide grains were disappeared after the thermal development.

In a case in which silver bromide or the silver halide grain having a low iodine content of about 3.5 mol% was used, even when the silver iodide complex forming agent was incorporated, the grain remained without being disappeared and, accordingly, the transmission density was least reduced. It is apparent that an effect of the invention can be realized only when the high silver iodide grain and the silver iodide complex forming agent are used in combination.

[0505]

Example 2

## 1. Back Layer

### 1) Preparation of Coating Solution for Back Layer

(Preparation of Solid Fine Grain Dispersion (a) of Base Precursor)

64 g of a base precursor compound-1, 10 g of DEMOL N (trade name; manufactured by Kao Corporation), 28 g of diphenylsulfone, and 220 ml of distilled water were mixed. The resultant mixture was dispersed by using beads media by means of 1/4 G Sand-Grinder Mill (manufactured by Imex Co., Ltd.) to obtain a solid fine grain dispersion (a) of the base precursor compound having an average grain diameter of 0.2  $\mu\text{m}$ .

[0506]

(Preparation of Dye Solid Fine Grain Dispersion (a))

9.6 g of a cyanine dye compound-1, 5.8 g of sodium p-dodecyl sulfonate, and 305 ml of distilled water were mixed. The resultant mixture was dispersed by using beads media by means of a 1/4 G Sand-Grinder Mill (manufactured by Imex Co., Ltd.) to obtain a dye fine grain dispersion (a) having an average grain diameter of 0.2  $\mu\text{m}$ .

[0507]

(Preparation of Coating Solution for Antihalation Layer)

17 g of gelatin, 9.6 g of polyacrylamide, 70 g of the above-prepared solid fine grain dispersion (a) of base precursor,

56 g of the above-prepared dye solid fine grain dispersion (a), 1.5 g of monodispersed fine grains of polymethyl methacrylate (average grain size: 8  $\mu$ m; standard deviation of grain diameter: 0.4), 0.03 g of benzisothiazolinone, 2.2 g of sodium polyethylene sulfonate, 0.2 g of a blue dye compound-1, 4.2 g of an ultraviolet light-absorbing agent, and 844 ml of water were mixed to prepare a coating solution for an antihalation layer.

[0508]

(Preparation of Coating Solution for Back Surface Protective Layer)

In a vessel maintained at 40°C, 50 g of gelatin, 0.2 g of sodium polystyrene sulfonate, 2.4 g of N,N-ethylene bis(vinyl sulfonacetamide), 1 g of sodium t-octylphenoxyethoxyethane sulfonate, 30 mg of benzisothiazolinone, 37 mg of fluorine-type surfactant (F-1), 0.15 g of fluorine-type surfactant (F-2), 64 mg of fluorine-type surfactant (F-3), 32 mg of fluorine-type surfactant (F-4), 8.8 g of an acrylic acid/ethylacrylate copolymer (weight ratio of copolymerization: 5/95), 0.6 g of Aerosol OT (manufactured by American Cyanamid Company), 1.8 g of a liquid paraffin emulsion in terms of liquid paraffin, and 950 ml of water were mixed to prepare a coating solution for back surface protective layer.

[0509]

## 2) Coating of Back Layer

On a back surface side of the thus-undercoated support, the coating solution for the antihalation layer was applied such that a coated quantity of the solid fine grain dye was allowed to be  $0.04 \text{ g/m}^2$ , and the coating solution for the back surface protective layer was applied in a simultaneous multi-layer manner such that a coated quantity of the gelatin was allowed to be  $1.7 \text{ g/m}^2$  and, then, dried to prepare a back layer.

[0510]

## 2. Image-forming layer, Intermediate Layer, and Surface Protective Layer

### 2-1. Preparation of Material

#### 1) Preparation of Photosensitive Silver Halide Emulsions G to K

Tabular emulsion grains G to K having different average grain sizes from one another as shown in Table 3 were prepared in a same manner as in the preparation of the emulsion D of Example 1 except for appropriately changing a quantity of a 5% by mass methanol solution of 2,2'-(ethylenedithio)diethanol to be added, a temperature at the time of grain-forming, and an adding time of the solution A. Emulsion grains G and H are Comparative Examples.

[0511]

2) Preparation of Photosensitive Silver Halide Emulsions L to N

Further, for the comparison purpose, tabular silver bromide emulsions L to N were prepared as shown below.

[0512]

(Preparation of Tabular Silver Bromide Emulsion L)

(Grain formation)

1178ml of an aqueous solution containing 0.8 g of KBr, and 3.2 g of gelatin, subjected to an oxidation treatment, having an average molecular weight of 20000 were stirred while keeping it at 35°C. Respective solutions of 1.6 g of silver nitrate, 1.16 g of KBr, and 1.1 g of gelatin subjected to the oxidation treatment were added to the thus-stirred solution by a triple-jet method consuming 45 seconds. A concentration of silver nitrate in the resultant mixture was 0.3 mol/L. The mixture was heated up to 76°C consuming 20 minutes and, then, added with 26 g of succinated gelatin having an average molecular weight of 100000 and, thereafter, added with an aqueous solution containing 209 g of silver nitrate and an aqueous KBr solution while keeping a pAg value at 8.0 and accelerating a flow rate by a controlled-double-jet method consuming 75 minutes. After being added with gelatin having an average molecular weight of 100000, the resultant mixture was desalted in accordance

with an ordinary method and, then, added with gelatin having an average molecular weight of 100000 while allowing it to be dispersed and, thereafter, adjusted so as to have a pH value of 5.8 and a pAg value of 8.0 at 40°C, thereby obtaining an emulsion. It is found that the thus-obtained emulsion contained one mol of silver and 40 g of gelatin based on 1 kg of the emulsion and that silver halide grains therein were tabular grains having an average projected area diameter of 0.97  $\mu\text{m}$ , a variation coefficient of projected area diameter of 19.1%, an average thickness of 0.12  $\mu\text{m}$ , and an average aspect ratio of 8.1.

[0513]

(Chemical Sensitization)

Each emulsion thus prepared was subjected to chemical sensitization while kept stirring at 56°C. Firstly, the emulsion was added with  $1 \times 10^{-4}$  mol, based on 1 mol of silver halide, of a thiosulfonic acid compound-1 to be described below and, then, added with 0.15 mol%, based on an entire silver quantity, of AgI grains having a size of 0.03  $\mu\text{m}$ . 3 minutes after such addition, the resultant mixture was added with  $1 \times 10^{-6}$  mol/Ag mol of thiourea dioxide and kept to stand for 22 minutes as it was to allow a reduction sensitization to be performed. Next, the thus-reduction-sensitized mixture was added with  $3 \times 10^{-4}$  mol equivalent, based on 1 mol of silver halide, of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene,  $1 \times$



$10^{-3}$  mol equivalent, based on 1 mol of silver halide and in terms of a quantity of a sensitizing dye IV-I, of a sensitizing dye IV-I dispersion,  $1 \times 10^{-4}$  mol equivalent, based on 1 mol of silver halide, of each of sensitizing dyes-1 and -2 to be described below and calcium chloride.

[0514]

Subsequently, the resultant mixture was added with  $6 \times 10^{-6}$  mol equivalent, based on 1 mol of silver halide, of sodium thiosulfate and  $4 \times 10^{-6}$  mol equivalent, based on 1 mol of silver halide, of a selenium compound-1 and, then, added with  $2 \times 10^{-3}$  mol equivalent, based on 1 mol of silver halide, of chloroauric acid and, thereafter, added with 67 mg equivalent, based on 1 mol of silver halide, of nucleic acid (trade name: RNA-F; manufactured by Sanyo-Kokusaku Pulp Co., Ltd.). 40 minutes after such addition, the resultant mixture was added with  $1 \times 10^{-4}$  mol equivalent, based on 1 mol of silver halide, of a water-soluble mercapto compound-1 and, then, cooled to terminate the chemical sensitization of the emulsion L.

[0515]

(Preparation of Tablular Silver Bromide Emulsions M and N)

Emulsions M and N were prepared in a same manner as in the emulsion L except for adjusting the pAg value at the time of being performed by the controlled-double-jet method, and

temperatures at the time of nucleus formation and grain growth.  
A quantity of the chemical sensitizer was adjusted so as to  
be optimal for each grain.

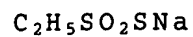
[0516]

[Table 3]

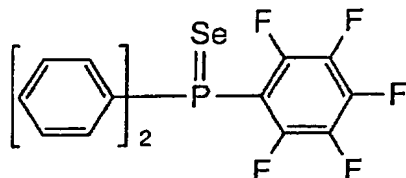
Emulsion	Halogen composition	Average projected area diameter ( $\mu\text{m}$ )	Variation coefficient of Average projected area	Average grain thickness ( $\mu\text{m}$ )	Average aspect ratio	Average sphere equivalent diameter ( $\mu\text{m}$ )	Remark
G	AgI	0.037	8.2	0.031	1.2	0.04	Comparative Example
H	AgI	0.330	13.5	0.094	3.5	0.25	Comparative Example
I	AgI	0.960	19.5	0.120	8.0	0.55	Present Invention
J	AgI	1.650	19.8	0.103	16.0	0.75	Present Invention
K	AgI	2.580	23.1	0.086	30.0	0.95	Present Invention
L	AgBr	0.970	19.1	0.120	8.1	0.55	Comparative Example
M	AgBr	1.670	19.5	0.104	16.0	0.76	Comparative Example
N	AgBr	2.620	22.1	0.087	30.0	0.96	Comparative Example

[0517]

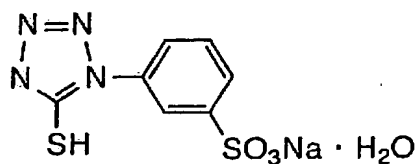
Thiosulfonic acid compound-1



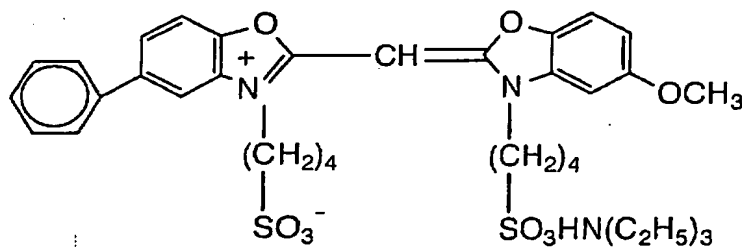
Selenium compound-1



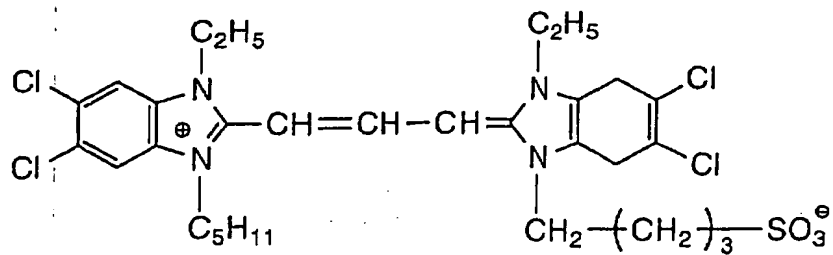
Water-soluble mercapto compound-1



Sensitizing dye-1



Sensitizing dye-2



[0518]

(Preparation of Silver Halide Emulsion for Preparation of Coating Solution)

The above-described silver halide dispersion was dissolved at 40°C and, then, added with  $7 \times 10^{-3}$  mol, based on 1 mol of silver, of a 1% by mass aqueous solution of benzothiazolium iodide and, thereafter, added with water such that a silver halide content thereof, based on 1 kg of a mixed emulsion for a coating solution, is allowed to be 38.2 g in terms of silver and, then, added with a 1-(3-methylureidophenyl)-5-mercaptotetrazole such that the content thereof is allowed to be 0.34 g based on 1 kg of the mixed emulsion for the coating solution and, further, added with each of compounds 2, 20 and 26, as "a compound in which a one-electron-oxidized form generated by oxidizing one electron therein can release one or more electrons", such that each of the compounds is allowed to be  $2 \times 10^{-3}$  mol based on 1 mol of silver of silver halide and, still further, added with each of compounds (19), (49) and (71), as a compound having an adsorptive group and a reducing group, such that each of the compounds is allowed to be  $8 \times 10^{-3}$  mol based on 1 mol of silver halide.

[0519]

2) Preparation of Pigment-1 Dispersion

250 g of water was added to 64 g of C.I. Pigment Blue

60 and 6.4 g of DEMOL N (manufactured by Kao Corporation). Then, the resultant mixture was thoroughly mixed to form a slurry. 800 g of zirconia beads having an average diameter of 0.5 mm was prepared and charged in a vessel together with the slurry. The slurry was dispersed for 25 hours with a dispersing machine (1/4 G Sand-Grinder Mill manufactured by Imex Co., Ltd.) and, then, taken out of the vessel and, thereafter, added with water to allow a concentration of such pigment to be a 5% by mass, thereby obtaining a pigment-1 dispersion. Pigment grains contained in the thus-obtained pigment dispersion had an average grain diameter of 0.21  $\mu\text{m}$ .

[0520]

### 3) Preparation of Coating Solution

(Preparation of Coating Solution for Image-Forming Layer)

1,000 g of the above-described fatty acid silver salt dispersion A, 104 ml of water, 35 g of a pigment-1 dispersion, 6.3 g of an organic polyhalogen compound dispersion a, 20.7 g of an organic polyhalogen compound dispersion b, 1,060 g of and SBR Latex (Tg: 17°C) solution, 75 g of a reduction agent-1 dispersion, 75 g of a reduction agent-2 dispersion, 106 g of a hydrogen-bonding compound-1 dispersion, 4.8 g of a development accelerator-1 dispersion, 9 ml of a mercapto compound-1 aqueous solution, and 27 ml of a mercapto compound-2 aqueous solution were mixed by adding them in the stated order. The resultant

mixture was further added with 9 g of a mercapto compound-1 solution and silver iodide complex forming agent (shown in Table 4) and, immediately before coating, added with a silver halide coating solution (shown in Table 4) such that a quantity thereof was allowed to be 0.25 mol in terms of silver, based on 1 mol of fatty acid silver salt (0.125 mol in regard to the sample 2-9; 0.5 mol in regard to the sample 2-11) and, thereafter, thoroughly mixed. The resulting coating solution for the image-forming layer was fed to a coating die as it was such that a coated quantity of silver was allowed to be  $1.65 \text{ g/m}^2$  as a sum of the fatty acid silver salt and the silver halide.

[0521]

An intermediate layer, a first layer of a surface protective layer, and a second layer of the surface protective layer used same layers as in the Example 1, respectively.

[0522]

2-2. Preparation of Photothermographic Materials 2-1 to 2-25

[0523]

On a surface opposite to a back surface, an image-forming layer, an intermediate layer, a first layer of a surface protective layer, and a second layer of the surface protective layer were coated in the stated order in a simultaneous

multi-layer manner by using a slide bead coating method to prepare samples of photothermographic materials.

Temperatures, at that time, of coating solutions were adjusted such that the coating solution for the image-forming layer and that for the intermediate layer were maintained at 35°C, that for the first layer of the surface protective layer was maintained at 36°C and that for the second layer of the surface protective layer was maintained at 37°C.

[0524]

Coating and drying conditions are described below.

Coating was performed at a coating speed of 160 m/min. A distance between the tip of the coating die and the support was set in a range from 0.10 mm to 0.30 mm. Pressure inside a reduced pressure chamber was set lower than the atmospheric pressure by from 196 Pa to 882 Pa. The support was electrically discharged with ionized air before coating.

After the coated solution was chilled in a subsequent chilling zone with air having a dry bulb temperature of from 10°C to 20°C, the coated support was transported to a helical non-contact-type drying apparatus in a non-contact manner and, then, dried therein with drying air having a dry bulb temperature of from 23°C to 45°C and a wet bulb temperature of from 15°C to 21°C to obtain coated samples 21 to 27.

After such drying, the thus-obtained samples were



conditioned in moisture contents at 25°C from 40% to 60% RH and, then, heated such that a temperature of each of surfaces thereof came to be from 70°C to 90°C and, subsequently, cooled such that the temperature of a surface of a film came to be 25°C.

[0525]

### 3. Evaluation of Photographic Performance

#### (Preparation)

Each of the thus-obtained samples was cut into pieces of a half-size, wrapped with the above-described wrapping material in an atmosphere of 25°C 50% RH and, then, stored for 2 weeks at room temperature.

#### (Wrapping Material)

The wrapping material used was 50  $\mu\text{m}$  thick polyethylene film comprising PET: 10  $\mu\text{m}$ /PE: 12  $\mu\text{m}$ /aluminum foil: 9  $\mu\text{m}$ /Ny: 15  $\mu\text{m}$  /PE: 50  $\mu\text{m}$  containing 3% by mass of carbon. Oxygen transmittance was 0.02 ml/atm·m<sup>2</sup>·25°C·day; and moisture transmittance was 0.10 g/atm·m<sup>2</sup>·25°C·day.

[0526]

The above-described photothermographic material was assessed as mentioned below.

#### (Exposure of Photothermographic Material)

The photothermographic material was subjected to an

exposure treatment in a manner as described below.

The Fuji Medical Dry Laser Image FM-DPL was modified and, then, performed exposure and development processes. The exposure was conducted by irradiating such photosensitive material by a semiconductor laser (NLHV 3000E manufactured by Nichia Corporation; oscillation wavelength: 405 nm) by restricting a beam diameter to 100  $\mu\text{m}$  X 100  $\mu\text{m}$ . The exposure was conducted by changing irradiation quantities of a laser in steps. The development was conducted by means of a thermal development part of the FM-DPL, while using 4 plates of panel heaters therein which have been set at 112°C, 119°C, 121°C, and 121°C, respectively. An entire developing time was 24 seconds.

[0527]

(Evaluation of Sample)

Density of the resultant image was measured by using a Macbeth densitometer to construct a characteristic curve of the density to a logarithm of exposed quantity.

Sensitivity: Sensitivity was exhibited in terms of a reciprocal number of an exposed quantity necessary for providing a blackening density of fog plus 1.0 and was shown as a relative value assuming the sensitivity of Sample No. 2-13 to be 100; it shows that, as the value becomes larger, the sensitivity becomes higher.

Dmin: Density of a non-image part was measured by using

a Macbeth densitometer. The density thereof before thermal development was also measured.

[0528]

#### Evaluation of Degree of Haze

A degree of haze denotes a degree of diffusion of light which is incident in a photosensitive material and is shown as a percentage of a diffused transmitted light quantity against an entire transmitted light quantity. The degree of haze was measured by using a haze meter "Model 1001DP" manufactured by Nippon Denshoku Industries Co., Ltd.

[0529]

#### Evaluation of Image Storability (Printout)

An image sample obtained by thermally developing each of samples 1-13 to 1-38 was exposed to fluorescent light having an intensity of 8500 lux in an atmosphere of 40°C 50% RH for 3 days. An optical density of an unexposed part of the thus-exposed image sample was measured. The thus-measured optical density was defined as  $D_{min_2}$  and that before such exposure to the fluorescent light was defined as  $D_{min_1}$ . A difference ( $\Delta D_{min}$ ) was obtained by the following equation:

$$\Delta D_{min} = D_{min_2} - D_{min_1}.$$

[0530]

[Table 4]

(Present Inv.: Present invention, CE: Comparative example)

Sample No.	Emulsion No.	Silver iodide complex forming agent		Haze degree of film		Photographic property		Image storability		Remark
	Emulsion No.	Addition quantity	Compound No.	Addition quantity	Before development	After development	Dmin (before development)	Sensitivity	Printout	
2-1	G	0.25	-	-	28.6	22.5	0.18	No image	0.05	CE
2-2	H	0.25	-	-	42.5	36.6	0.22	No image	0.07	CE
2-3	I	0.25	-	-	50.5	45.6	0.24	No image	0.08	CE
2-4	J	0.25	-	-	52.4	46.1	0.26	No image	0.10	CE
2-5	K	0.25	-	-	58.5	52.6	0.27	No image	0.11	CE
2-6	L	0.25	-	-	50.2	44.3	0.25	No image	0.52	CE
2-7	M	0.25	-	-	53.5	47.5	0.28	No image	0.63	CE
2-8	N	0.25	-	-	57.2	51.2	0.28	No image	0.88	CE
2-9	G	0.125	F-444	8 mol%	28.6	22.5	0.18	0.03	0.00	CE
2-10	ditto	0.25	ditto	8 mol%	28.8	22.6	0.18	0.03	0.00	CE
2-11	ditto	0.5	ditto	8 mol%	29.2	23.0	0.18	0.04	0.00	CE
2-12	H	0.25	ditto	8 mol%	42.5	23.2	0.17	9	0.01	CE
2-13	I	0.25	ditto	8 mol%	50.5	24.1	0.18	100	0.02	Present inv.
2-14	J	0.25	ditto	8 mol%	52.4	24.2	0.18	253	0.02	Present inv.
2-15	K	0.25	ditto	8 mol%	58.5	23.8	0.28	515	0.02	Present inv.
2-16	L	0.25	ditto	8 mol%	50.2	44.3	0.31	120	1.08	CE
2-17	M	0.25	ditto	8 mol%	53.5	47.5	0.31	317	1.22	CE
2-18	N	0.25	ditto	8 mol%	57.2	51.2	0.20	638	1.52	CE
2-19	G	0.25	F-431	9.5 mol%	28.6	23.2	0.17	0.03	0.00	CE
2-20	H	0.25	ditto	9.5 mol%	42.5	24.1	0.18	7.7	0.01	CE
2-21	I	0.25	ditto	9.5 mol%	50.5	24.4	0.18	85	0.02	Present inv.
2-22	J	0.25	ditto	9.5 mol%	52.4	24.2	0.19	215	0.02	Present inv.
2-23	K	0.25	ditto	9.5 mol%	58.5	23.2	0.17	438	0.02	Present inv.
2-24	L	0.25	ditto	9.5 mol%	50.2	44.3	0.30	102	1.21	CE
2-25	M	0.25	ditto	9.5 mol%	53.5	47.5	0.33	269	1.42	CE
2-26	N	0.25	ditto	9.5 mol%	57.2	51.2	0.33	542	1.68	CE

[0531]

The obtained results are shown in Table 4. From the results shown in Table 4, following facts are found:

1) an image in which sensitivity is high,  $D_{min}$  is low, and clearness of a film is favorable can be obtained by simultaneously using the silver halide emulsion, being the silver iodide emulsion, having a size as large as  $0.3 \mu m$  or more and the silver iodide complex forming agent according to the invention;

2) Only a small increase of sensitivity can be expected even when a quantity of the fine grain silver iodide emulsion having a size of  $0.25 \mu m$  or less is increased. To contrast, a high sensitivity can only be obtained by using the emulsion having a size as large as  $0.3 \mu m$  or more according to the invention;

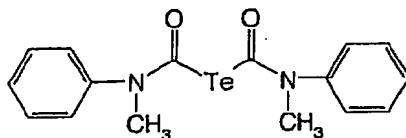
3) In regard to the emulsion having a size as large as  $0.3 \mu m$  or more, the haze of the film before the thermal development is extremely high. However, the haze thereof after the thermal development is decreased by virtue of the silver iodide complex forming agent according to the invention and, accordingly, the film comes to be clear and is also excellent in the image storability (printout property); and



4) A silver bromide grain having a size of  $0.3 \mu m$  or more has a sufficient sensitivity as a photosensitive material for photo-taking. However, since a dissolution phenomenon of the silver halide grain will not occur by the silver iodide complex

[ 0 5 3 2 ]

[ 0 5 3 3 ]

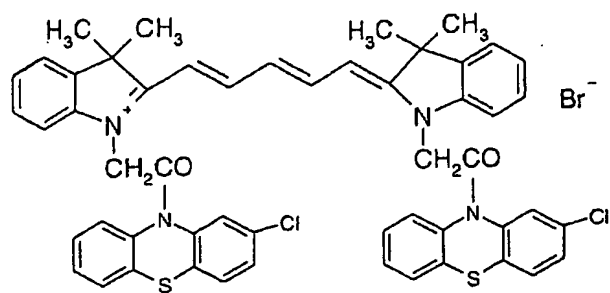
Tellurium sensitizer C


$$\begin{array}{c} \text{H} \\ | \\ \text{C}_2\text{H}_5-\text{N}^+=\text{C}-\text{NH}-\text{C}_2\text{H}_4-\text{NH}-\text{C}=\text{N}^+-\text{C}_2\text{H}_5 \\ | \qquad \qquad \qquad | \\ \text{C}_2\text{H}_5-\text{N}-\text{H} \qquad \qquad \qquad \text{N}-\text{C}_2\text{H}_5 \\ | \\ \text{H} \end{array}$$

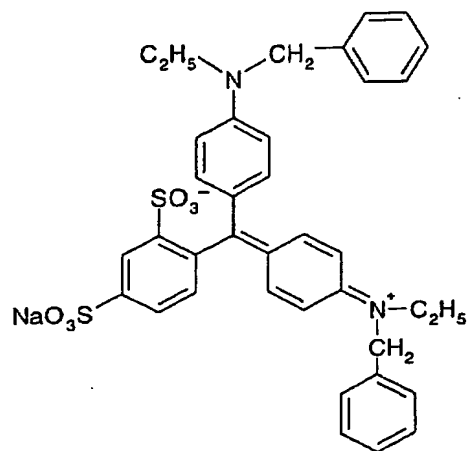
(  -SO<sub>2</sub>- -SO<sub>2</sub>CH<sub>2</sub>COO<sup>-</sup> )

[Formula 59]

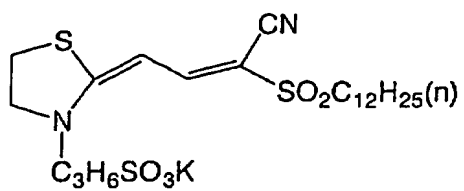
Cyanine dye Compound-1



Blue dye compound-1



Ultraviolet light-absorbing agent-1

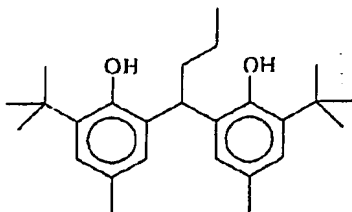




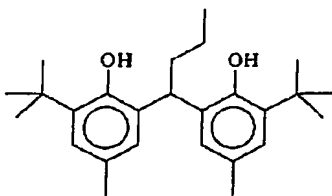
[0535]

[Formula 60]

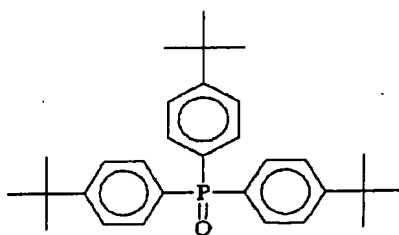
(Reduction agent-1)



(Reduction agent-2)

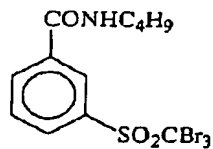
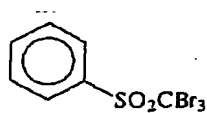


(Hydrogen bond-forming compound-1)



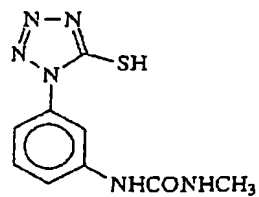
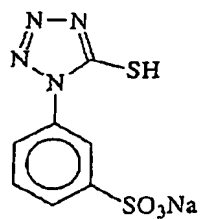
(Polyhalogen compound-1)

(Polyhalogen compound-2)



(Mercapto compound-1)

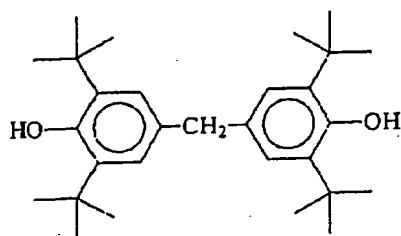
(Mercapto compound-2)



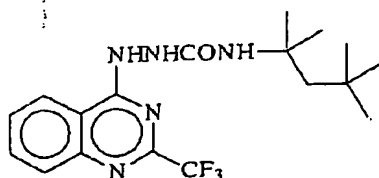
[0536]

[Formula 61]

(Color tone adjusting agent-1)



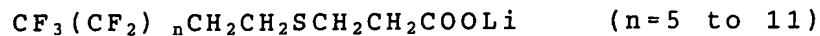
(Development accelerator-1)



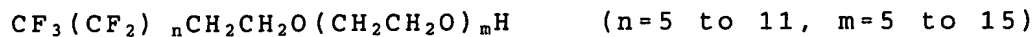
[0537]

[Formula 62]

(F-1) Mixture of

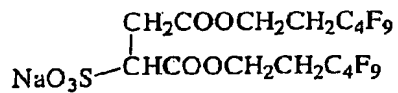
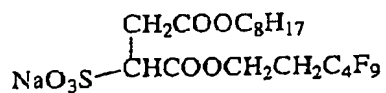


(F-2) Mixture of



(F-3)

(F-4)



[0538]

Example 3

1) Support

Undercoat having the prescription of Example 1 was applied on each surface of a PET support, having a thickness of 175  $\mu\text{m}$ , colored in blue with a blue dye (1,4-bis(2,6-diethylanilinoanthraquinone)).

[0539]

## 2) Preparation of Coated Sample

An image-forming layer, an intermediate layer, a first layer for a surface protection layer, and a second layer for the surface protection layer having the same composition as that of the samples 2-14 of Example 2 were applied on each side of a support in a simultaneous manner and, then, dried. In other words, a photothermographic material, having a total coated quantity of silver of  $3.3 \text{ g/m}^2$ , in which an image-forming layer having a coated quantity of silver of  $1.65 \text{ g/m}^2$  as a sum of a fatty acid silver and a silver halide was applied on each side of the support was prepared.

[0540]

## 3) Evaluation of Performance

The thus-prepared photosensitive material in which both sides were coated was evaluated as described below.

A sample thereof was sandwiched between two sheets of X-ray regular screen HI-SCREEN B3 (manufactured by Fuji Photo Film Co., Ltd.) ( $\text{CaWO}_4$  having a luminescent peak wavelength

of 425 nm being used as a phosphor) to construct a combined system for image-forming. The combined system was subjected to an X-ray exposure for 0.05 second to perform an X-ray sensitometry. An X-ray apparatus DRX-3724HD (trade name; manufactured by Toshiba Corporation), as well as a tungsten target, was used. An X-ray which was emitted by applying an electric potential of 80 kVp to the apparatus by means of a three-phase pulse generator and, then, allowed to pass through a filter of water in 7 cm thick which has absorption approximately equivalent to that of a human body was employed as a light source. An exposure was conducted in a stepwise manner at a width of  $\log E = 0.15$  by changing exposure quantities of the X-ray by means of a distance method. After the exposure, a thermal treatment was performed on the thus-exposed sample under thermal development conditions as described below to obtain an image. The thus-obtained image was evaluated by using a densitometer.

[0541]

A thermal development part of the Fuji medical dry laser imager FM-DP L (manufactured by Fuji Photo Film Co., Ltd.) was modified such that heating can be performed from both sides to fabricate a thermal developing machine. Further, another medication was conducted such that a transportation roller of the thermal development part was replaced by a heat drum so as to allow a film sheet to be transported. Temperatures of

4 panel of a panel heater were set at 112°C, 118°C, 120°C and 120°C, respectively while a temperature of the heat drum was set at 120°C. Further, a transportation speed was increased and set at 14 seconds in total.

[0542]

On the other hand, a regular photosensitive material RX-U (manufactured by Fuji Photo Film Co., Ltd.) of a wet-type developing system was exposed under same conditions as described above and, then, treated with a developing solution CE-DI (manufactured by Fuji Photo Film Co., Ltd.) by using an automatic developing machine CEPROS-M2 (manufactured by Fuji Photo Film Co., Ltd.) for 45 seconds.

The photographic characteristics of the image obtained by the photothermographic material according to the invention and those of the image obtained by the wet-type developing system were compared with each other. As a result, both of them are equally favorable.

[0543]

#### Example 4

##### 1) Preparation of Sample

A double-side-type photographic material was prepared in a same manner as in Example 3 except for two points. The two points of alterations from Example 3 are as follows:

(1) An emulsion K was used as a silver halide emulsion and an ortho spectral sensitization was optimally conducted by sensitizing dyes 1 and 2; and

(2) A cross-over cut layer was provided between an image-forming layer and a support.

[0544]

(Preparation of Coating Solution for Cross-Over Cut Layer)

17 g of polyvinyl alcohol PVA-205 (manufactured by Kuraray Co., Ltd.), 9.6 g of polyacrylamide, 70 g of a solid fine grain dispersion (a) of a base precursor as described in Example 2, 56 g of an ortho dye solid fine grain dispersion (dye solid content: 3%; being prepared in a same manner as in the dye solid fine grain dispersion as in Example 2) containing an ortho thermally decolorizable dye-1 ( $\lambda_{\max}=566$  nm) as described in JP-A No. 11-231457, 0.03 g of benzisothiazolinone, 2.2 g of sodium polyethylene sulfonate and 844 ml of water were mixed to prepare a coating solution for a cross-over cut layer.

[0545]

(Preparation of Coated Sample)

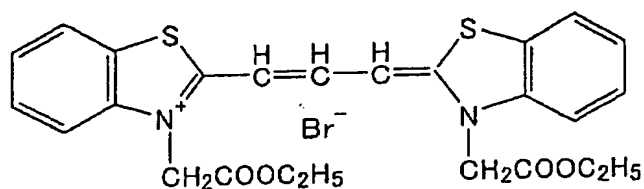
A cross-over cut layer, an image-forming layer, an intermediate layer, a first layer for a surface protective layer, and a second layer for the surface protective layer were applied on each side of a support in a simultaneous manner and, then,

dried. A flow rate of the cross-over cut layer was adjusted such that a coated quantity of the solid content of the ortho thermally decolorizing dye was allowed to be 0.04 g/m<sup>2</sup>. Coating quantities of other layers were allowed to be same as those in Example 3.

[0546]

Ortho thermally decolorizing dye-1

[Formula 63]



[0547]

## 2) Evaluation of Performance

An X-ray exposure and thermal development were conducted in a same manner as in Example 3, except for using an X-ray ortho screen HG-M (manufactured by Fuji Photo Film Co., Ltd.) as a fluorescent screen (a terbium-activated gadolinium oxysulfide phosphor being used as a phosphor; a luminescent peak wavelength: 545 nm).

[0548]

On the other hand, a photosensitive material SHR-S30 (manufactured by Fuji Photo Film Co., Ltd.) for an ortho system

was exposed under same conditions as described above and, then, treated with a processing solution CE-DI-M2 (manufactured by Fuji Photo Film Co., Ltd.) by using an automatic developing machine CEPROS-M2 (manufactured by Fuji Photo Film Co., Ltd.) for 45 seconds to form an image.

The photographic characteristics of the thus-formed image obtained by using the photosensitive material and those of the image obtained by using the former photosensitive material according to the invention were compared with each other. As a result, both of them are equally favorable.

A measurement of sensitivity was performed in a same manner as in Example 1 of Japanese Patent No. 3083647 except for performing development by thermal development processing. As a result, the sensitivity was 0.0076 lux-second.

A measurement of cross-over was performed in a same manner as in Example 1 of JP-A No. 11-142723 except for performing development by thermal development processing. As a result, the cross-over was 7%.

[0549]

#### Example 5

##### 1) Preparation of Sample

A single-side-type photosensitive material was prepared in a same manner as in Example 2.

However, the image-forming layer was applied in two layers,



namely, an upper layer and a lower layer and coated silver quantity as an entire silver quantity of fatty acid silver halide of each of these layers was allowed to be  $0.8 \text{ g/m}^2$ . The silver halides which were used for the upper layer and the lower layer were an emulsion I and an emulsion J, respectively. Ortho spectral sensitization of the upper layer and the lower layer was optimally performed by using the sensitizing dyes 1 and 2.

Further, the dye solid fine grain dispersion to be used in a coating solution for the antihalation layer which is a back layer was replaced by the dye solid dispersion of the ortho thermally decolorizing dye in Example 4.

[0550]

## 2) Evaluation of Performance

The thus-obtained ortho sensitizing single-side-type photosensitive material was evaluated as described below.

A fluorescent screen for mammography UM MAMMO FINE (manufactured by Fuji Photo Film Co., Ltd.) (a terbium-activated gadolinium oxysulfide phosphor being used as a phosphor; a luminescent peak wavelength: 545 nm) was used as a fluorescent screen. Surfaces of the image-forming layer of the sample and the protective layer of the screen were allowed to be in contact with each other and a resultant combined body was inserted in a cassette ECMA (manufactured by Fuji Photo Film Co., Ltd.).

The X-ray tube, an upper lid of the cassette, the film, and the screen were aligned in the stated order and were subjected to the X-ray irradiation.

[0551]

A commercially available machine for mammography DRX-B1356EC (manufactured by Toshiba Corporation) was used as an X-ray supply. The X-ray which was emitted from an Mo target tube operated by 26 kVp generated by means of three-phase electric supply and allowed to pass through 1 mm-thick Be, 0.03 mm-thick Mo and a 2 cm-thick filter made of acrylate was used. An exposure was conducted for one second in a stepwise manner at a width of  $\log E = 0.15$  by varying the exposure quantity of the X-ray by means of a distance method.

After such exposure, thermal development processing was performed in a same manner as in Example 2.

[0552]

On the other hand, a photosensitive material for mammography UM-MA<sub>Hc</sub> (manufactured by Fuji Photo Film Co., Ltd.) was exposed under same conditions as described above and, then, treated with a processing solution CE-DI (manufactured by Fuji Photo Film Co., Ltd.) by using an automatic developing machine CEPROS-M2 (manufactured by Fuji Photo Film Co., Ltd.) for 90 seconds to form an image.

The photographic characteristics of the thus-formed image obtained by using the photosensitive material for mammography and those of the image obtained by using the former single-side-type photosensitive material according to the invention were compared with each other. As a result, both of them are equally favorable.

[0553]

Sensitivity of the resultant photothermographic material was measured in a same manner as in Example as described in JP-A No. 10-62881 except for performing development by thermal development processing. As a result, the sensitivity was 0.021 lux-second. Further, gradation between density points of fog plus 0.25 and fog plus 2.0 was also measured. As a result, the gradation was 4.1.

[0554]

#### Example 6

A double-side-type photosensitive material was prepared in a same manner as in Example 3.

However, the support was changed into PEN (polyethylene naphthalate).

Commercially available polyethylene-2,6-naphthalate was melted at 300°C and, then, extruded from a T-type die and, thereafter, stretched up to 3.3 times in the machine direction

and up to 3.3 times in the transverse direction at 140°C and, subsequently, subjected to thermal fixation at 250°C for 6 seconds to obtain a roll of film having a thickness of 175  $\mu\text{m}$ . The support was treated with corona discharge by a solid-state corona discharge processor Model 6KVA (manufactured by Pillar Co.), in which the support having a width of 30 cm was treated at a running rate of 20 m/minute. From values of electric current and voltage read at that time, it was found that a treatment of 0.375 KV-A·min/m<sup>2</sup> was applied to the support. A discharge frequency at the time of the treatment was 9.6 KHz and a gap clearance between an electrode and a dielectric roll was 1.6 mm. Undercoat was performed in a same manner as in that of the support in Example 1.

[0555]

The resultant double-side-type photothermographic material was evaluated as described below.

Each side of a sample of the double-side-type photosensitive material and a sheet of Ultravision First Detail (manufactured by Du Pont) were allowed to be in contact with each other and, then, exposed to the X-ray for 0.05 second to perform X-ray sensitometry. An exposure quantity of the X-ray was adjusted by varying a distance between the X-ray tube and the cassette.

After such exposure, a thermal development process was

performed on the sample in a same manner as in Example 3.

As a result, a same excellent image as that in Example 3 was obtained.

[0556]

[Effects of the Invention]

The present invention provides a photothermographic material and an image forming method using the photothermographic material. The photothermographic material has high sensitivity and little haze of a film after thermal development, whereby a clear image is obtained.

[BRIEF DESCRIPTION OF THE DRAWINGS]

[Fig. 1]

Fig. 1 shows an electron micrograph of a silver iodide emulsion according to the present invention.

[Fig. 2]

Fig. 2 shows spectral absorption spectra of photothermographic materials according to the invention before and after thermal development in which a solid line indicates absorption spectra before the thermal development while a broken line indicates absorption spectra after the thermal development.

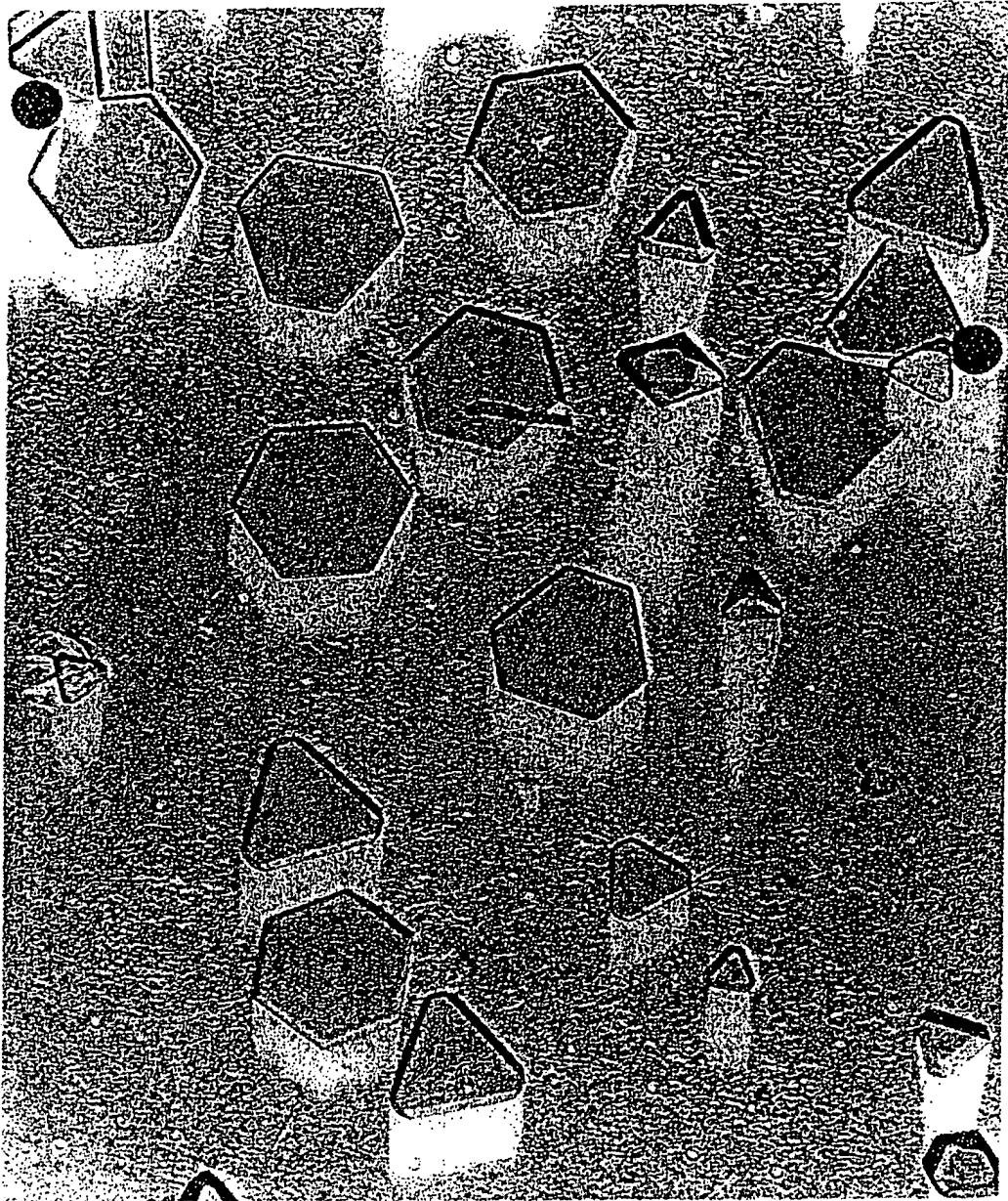
[Fig. 3]

(A) and (B) show electron micrographs of ultrathin

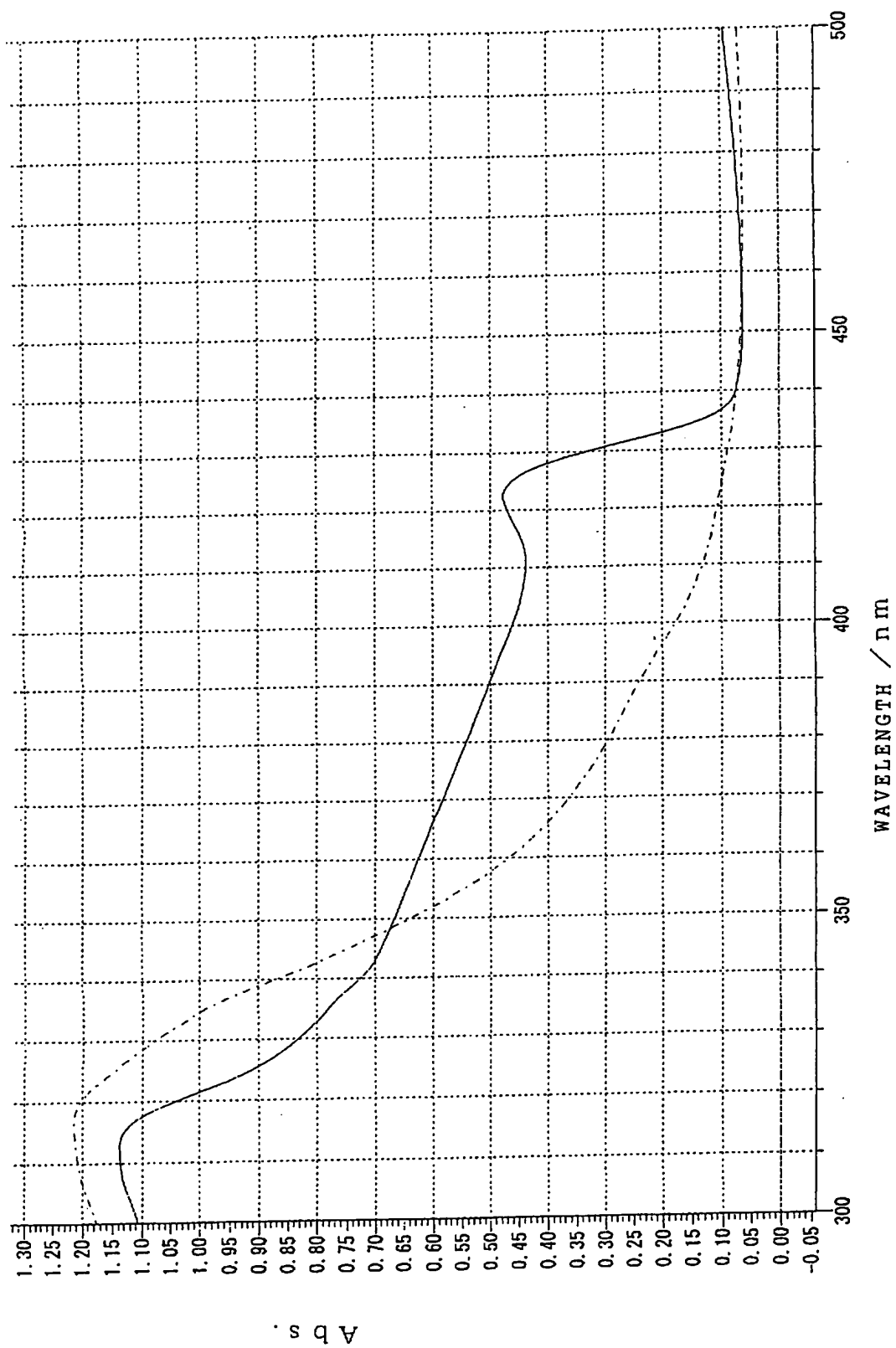
sections of photothermographic materials according to the invention before and after thermal development, respectively, in which micrograph (A) shows an electron micrograph of a specimen thereof before the thermal development and micrograph (B) shows an electron micrograph of a specimen thereof after the thermal development.

[DOCUMENT NAME] DRAWINGS

[FIG. 1]



[FIG. 2]

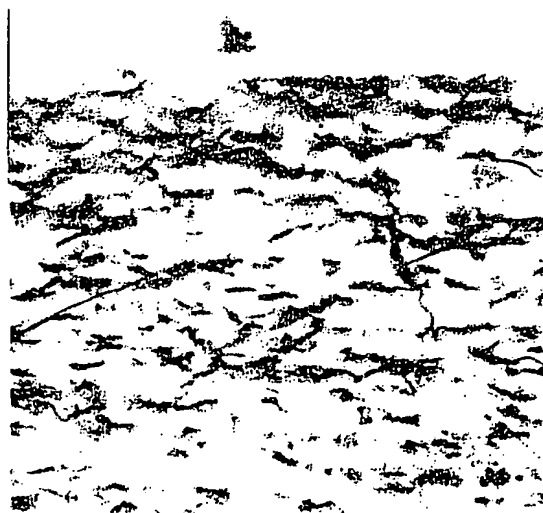




[FIG. 3]



Phot. A



Phot. B

[DOCUMENT NAME]      ABSTRACT OF DISCLOSURE

[SUMMARY]

[OBJECT]

An object of the invention is to provide a photothermographic material which has high sensitivity and excellent film transparency, and an image forming method.

[MEANS FOR SOLUTION]

A photothermographic material comprising, on a surface of a support, an image-forming layer comprising at least a photosensitive silver halide, a non-photosensitive organic silver salt, a reduction agent for a silver ion, and a binder, wherein: 1) a silver iodide content in the photosensitive silver halide is in a range from 40 mol% to 100 mol%; and 2) an average sphere-equivalent diameter of the photosensitive silver halide is in a range from 0.3  $\mu\text{m}$  to 5.0  $\mu\text{m}$ .

[SELECTED FIGURE]

None

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